Use of carbon isotope and C/N geochemistry in reconstructing vegetation communities: a mid- to late-Holocene palaeoenvironmental investigation from Romney Marsh, Kent, UK

Andrews, Jonathan Boyce

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Jonathan Boyce Andrews

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Declaration

This thesis, entitled:

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All of the work within this thesis has been completed by Jonathan Andrews, under supervision of Professor Antony Long (Durham University), Dr. Jeremy Lloyd (Durham University), Professor Melanie Leng (Nottingham University) and Martyn Waller (Kingston University).

For my mum

Abstract

The use of stable carbon isotope geochemistry and C/N ratios for coastal palaeoenvironmental reconstructions is a relatively new and under-researched field. This research seeks to understand the processes which govern the carbon isotope and C/N ratios of past and present vegetation communities, particularly alder carr and saltmarsh. Romney Marsh is a large, extensively studied reclaimed coastal wetland in south-east England containing a two-metre thick peat layer that formed between *c.* 5500-1500 cal. yrs BP. The palynological data from two mid- to late- Holocene cores, Hope Farm and Little Cheyne Court, allows comparison to the $\delta^{13}C$ and C/N data collected in this study. Ninety-three contemporary plant samples, 25 contemporary soil samples and 234 fossil peat samples were collected and analysed for their carbon isotope and C/N ratios.

The results show that contemporary alder carr woodland plant material have more negative $\delta^{13}C$ (–26‰ to –32‰) than saltmarsh plant material (–22.5‰ to –26‰). The C/N of the plant material from the sampled vegetation communities varied dependent on the type material collected. In general leaf material has lower C/N (around 20) than non-leaf material (between 50 and 80). In the fossil core, former raised bog, sedge fen, alder carr and saltmarsh communities, identified by pollen and microfossil remains, have been tested for $\delta^{13}C$ and C/N. There is evidence for post-depositional changes in the alder carr communities, with a negative shift of between 0.7‰ and 2.0‰ from the contemporary soil to fossil peat.

Three periods of increased higher water availability have been identified within the Little Cheyne Court core using $\delta^{13}C$, at 4600-4000; 3200-2700; and 2200-1500 cal. yrs BP. Spectral analysis has found evidence for cycles, with periodicities of 1005 and 1675 years. The research has also provided evidence for past environmental stress on the vegetation communities, including changes in precipitation and changes in local coastal conditions, principally relative sea level.

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Chapter 1: Introduction

1.1 Introduction, and the importance of a new technique

The coast has been the focal point for many palaeoclimatic and palaeoenvironmental investigations, providing important information about relative sea-level changes, changing coastal morphodynamics, and different environmental conditions. Traditional reconstructions have relied on interpreting the contents of deposits in coastal and wetland sites using lithological and micro- and macrofossil techniques that include pollen, diatoms and foraminifera. Although many of these techniques have been successful in coastal and wetland investigations, each of them have their own limitations. The most obvious of these is that in certain areas the micro- or macrofossil in question is simply not deposited or preserved. By the nature of biological material, certain types are preserved better in the fossil record. Equally some species are under-represented in the fossil record; *Salix, Lonicera* and *Ilex* spp. trees produce far less pollen than many other tree species such as *Betula* or *Alnus*, and are likely to be under represented in the fossil record (e.g., Pohl, 1937; Faegri and Iversen, 1975; Waller *et al.*, 1999). Other trees such as *Pinus* spp. produce pollen that can be dispersed over long distances and, therefore, even if present in the fossil record may be regionally rather than locally derived (e.g., Tyldesley, 1973). Although many of these problems can be addressed, they can still provide complications, and may lead to erroneous conclusions. The most robust investigations will therefore use a multi-proxy approach, using two or more environmental or climatic indicators, and will use information from more than one site to reconstruct the local environmental and climatic conditions.

There are some circumstances when even using a multi-proxy approach from a variety of biological material may not be sufficient to lead to robust conclusions. In general, due to the time-consuming nature of pollen, diatom and foraminifera identification, core sampling is not usually contiguous or necessarily high-frequency. A consequence of this is that short term environmental and climatic variability may not be revealed. Furthermore, some climatic and environmental stresses and conditions upon an environment may still not be revealed. This is because processes such as water stress to a vegetation community may not significantly impact the

pollen record, or because certain diatoms are able to survive in more saline or warmer conditions over short term periods.

To understand what other environmental processes may have been operating in the past, new techniques are emerging that include the use of isotope geochemistry. Isotope geochemistry has been used in a wide variety of situations often in conjunction with traditional techniques to provide further information about the climate or environment. Often more than one environmental variable is affecting the isotope ratio of a particular sample, such as occurs in carbon isotope geochemistry. The carbon isotope ratios of any particular sample are often complicated by a number of environmental processes, such as changes in atmospheric CO_2, precipitation, temperature, geology, and as well as post-depositional processes. Recent reviews of isotope geochemistry (e.g., Deines, 1980; Arthur *et al.*, 1983; Lamb *et al.*, 2006) provide helpful discussion of the relative contributions of these environmental processes, but there are a number of issues which are still not resolved.

One such issue, which will be investigated in this research project, is the relationship between the carbon isotope ratios and the vegetation community which they are supposed to be associated with. Perhaps surprisingly, there are relatively few studies that have compared the isotope ratios from contemporary vegetation communities in wetland environments to their fossil counterparts. Those that have simply focus on comparing terrestrial and saltmarsh communities which represent average 'end-members' to the isotope environmental gradient (e.g., Andrews *et al.*, 1998; Andrews *et al.*, 2000; Wilson *et al.*, 2005a, b; Allen *et al.*, 2007). As a result, there is a real need to investigate the terrestrial vegetation communities in more detail to determine whether each of these communities have distinct carbon isotope ratios. This technique can be aided by using total organic carbon/total nitrogen (C/N) ratios to determine the general plant material type.

Since this is a relatively new application of this technique it is crucial to independently test the robustness of the technique. In the case of carbon isotopes and C/N ratios, one way to achieve this is to compare the new proxies with existing reconstructions based on one or more established techniques. The most obvious

proxy to use in the case of vegetation communities is the palynological record. The selection of the site should be from an area containing a variety of vegetation communities, and also where there has been substantial research to verify the nature of the communities.

The potential for using carbon isotope geochemistry in this way is enormous. If successful, the technique of carbon isotope geochemistry could be used not only in the absence of a particular macrofossil or microfossil, but also to provide more information about the wetland processes of a particular area, such as coastal flooding, and climatic changes. Furthermore, in a biological context it will allow a better understanding of the influence of changing climatic changes on specific vegetation communities. New information of this type could also be used as a better way of conserving similar contemporary environments, and for more efficient coastal wetland management.

1.2 Aims and objectives

This aim of this thesis is therefore to explore the applicability of carbon isotope geochemistry to the reconstruction of past coastal wetlands. The study site is Romney Marsh, a large and intensively studied coastal wetland in southern England, at the eastern end of the English Channel (Figure 3.1). The objective of the work is to determine new proxy records from a prominent organic horizon (known locally as the "main marsh peat") that formed during the mid Holocene (from *c.* 6000 to 2000 calibrated years before present (cal. yrs BP)) (Long and Innes, 1995; Waller *et al.*, 1999).

The research aims to advance our understanding of the application of isotope geochemistry to palaeoenvironmental reconstruction in coastal wetlands, as well as promote an improved appreciation of the evidence for wetland change in the Romney Marsh area.

The aim of advancing our understanding of carbon isotope geochemistry will be explored by investigating the following objectives:

Objective 1

- *to review published and collect new data regarding the carbon isotope and C/N ratios of contemporary coastal wetlands and their soils.*
    - To accurately understand past processes it is necessary to understand present ones. The vegetation communities chosen for analysis in this study are selected specifically to provide a modern analogue for fossil communities inferred from pollen records derived from the Romney Marsh main marsh peat. The sampling strategy is designed to provide useful information about the relative contribution of particular species, and also of specific parts of the plant, such as twigs, leaves and roots. Comparisons between contemporary sites will demonstrate the degree of variability that may arise due to spatial variations in precipitation, geology, or other unknown processes.

Objective 2

- *to review published and collect new data regarding the carbon isotope and C/N ratios of fossil vegetation communities and their soils.*
    - This will be achieved by sampling cores which have previously been examined for their pollen and diatom content and have been radiocarbon dated. The cores used here are ones that formed the basis for a review of the vegetation history of Romney Marsh study area by Waller *et al.* (1999). Samples are analysed from a range of fossil palaeoenvironments that include saltmarsh, alder carr, poor fen and raised bog.

Objective 3

- *to compare the carbon isotope and C/N ratios of contemporary and fossil vegetation communities.*
    - To fully understand the environmental processes which operated in the fossil record, it is necessary to understand the processes which influence the carbon isotope and C/N ratios in the contemporary environment. Direct comparison of similar vegetation communities in the contemporary and fossil records will help to achieve this.

Objective 4

- *to investigate the effects of local coastal conditions, geology, and source atmospheric carbon on the carbon isotope and C/N ratios.*
    - High resolution contiguous sampling of the fossil cores will allow the change in carbon isotope geochemistry through time to be better understood. The effect of processes such as changes in local coastal conditions, geology and the source atmospheric carbon on the final carbon isotope and C/N ratio of plant material is poorly understood for the Holocene period. This investigation will therefore help to resolve some of these unknown processes.

Objective 5

- *to provide greater understanding of wetland dynamics in the Romney Marsh region.*
    - Using the data collected in this research, alongside the wealth of information already collated for the Romney Marsh depositional complex, this study will provide new information about the wetland processes which have occurred during the Holocene in relation to climate, vegetation succession and coastal change.

1.3 Thesis structure

Chapter 2 provides an insight into the uses of carbon isotope geochemistry and C/N ratios in terms of environmental reconstructions, and examines its use within wetland environments. It draws upon previous research to show how carbon isotopes and C/N ratios are used with both contemporary and fossil data sets.

The study site is introduced in Chapter 3. There is an explanation of the rationale for site selection in both the contemporary and fossil contexts. There is also discussion of the supplementary field sites which are used for comparative purposes.

Chapter 4 explains the sampling strategy of the project. This includes the sampling strategy of the fieldwork, explaining how vegetation variability within communities

is captured in the contemporary setting, the selection of fossil cores, and their sub-sampling, and the laboratory processes involved.

The following two chapters detail the results generated using the methods described in Chapter 4. Chapter 5 presents the contemporary data, showing variability and consistency between sites investigated, both in terms of this research and also previous research. Chapter 6 presents the data from the core records.

Chapter 7 discusses the new findings of Chapters 5 and 6, in particular the applicability of isotope geochemistry and C/N ratios in reconstructing coastal wetland terrestrial and marine vegetation communities. I also investigate the potential problems and limitations of the approach. This study is placed within a local, regional and global context, relating possible changes in the fossil core to climatic changes found in other investigations.

Chapter 8 concludes the thesis, outlining the successes and weaknesses, but more importantly providing ways in which the project could be advanced by future research.

Chapter 2: Use of carbon isotope ($\delta^{13}C$) and C/N ratios in palaeoenvironmental reconstructions

2.1. Introduction

This chapter explores the use of $\delta^{13}C$ and C/N as a tool for reconstructing environmental change in the Romney Marsh depositional complex. To critically evaluate the use of this relatively new tool, it is necessary to understand the processes which influence $\delta^{13}C$ and C/N. This is achieved by examining previous and ongoing research involving alternative applications for the techniques as well as those specifically involved in environmental reconstruction. Priority will be given to the sites within north-west Europe (since these will have broadly similar climatic conditions to the investigated sites), and also those investigations involving Holocene deposits, particularly peat. To conclude, this chapter explores various limitations and challenges to the project, and more importantly the ways in which the effects of these potential problems can be reduced.

2.2 Carbon isotope ($\delta^{13}C$) and C/N ratios

Carbon atoms can exist in three different forms, dependant upon the number of neutrons which they contain, and these are known as 'isotopes'. The three carbon isotopes are ^{12}C, ^{13}C and ^{14}C, and have 6, 7 and 8 neutrons within their nuclei respectively (and also six protons). Clearly having more neutrons in the nucleus will increase the mass of the atom, and so ^{13}C is isotopically heavier than ^{12}C, and ^{14}C is isotopically heavier than ^{13}C and ^{12}C. The two stable carbon isotopes are ^{12}C and ^{13}C, and form the basis for isotopic geochemistry reconstructions, while ^{14}C is radioactive, and the rate of decay of the atom is used as an indicator of age.

In the atmosphere these isotopes occur in different abundances, with ^{12}C being by far the most abundant, and ^{14}C being the least. Plants obtain the majority of their carbon from atmospheric CO_2, and through photosynthesis ultimately use this carbon to form plant material. In order to determine the carbon isotopic composition of plant material it is reconverted to CO_2, and expressed as the ratio between ^{13}C and ^{12}C. The first standard to be used originated from a limestone carbonate from South Carolina, USA, known as the Pee Dee Belemnite (PDB), however this has long since been

exhausted (Coplen, 1995. Various NBS standards now replace this as the international agreed standards, and these have been calibrated through PDB and thus data is still referred to as being on the Vienna PDB scale (VPDB). Throughout the literature there is a cross section of terms to describe the carbon isotopic ratio of a particular sample. Values which have more negative values for $\delta^{13}C$ are also described as ^{12}C enriched, isotopically lighter, more negative and depleted; while values which have less negative values for $\delta^{13}C$ are also described as ^{13}C enriched, isotopically heavier, less negative and enriched. For this research the $\delta^{13}C$ ratios will simply be described as more or less negative respectively.

Thus $\delta^{13}C = [R(sample)/R(standard)-1] \times 1000.$ [Equation 1]

In the above equation $R = {}^{13}C/{}^{12}C$, and the ratio between the sample and standard is multiplied by 1000 for convenience, and expressed in parts per thousand (‰).

2.3 The history and uses for carbon isotope geochemistry and C/N ratios

The history of carbon isotope geochemistry can be traced as far back as the late 1930s and early 1940s. Early research into the subject found systematic differences in the carbon isotopic ratios of living organic matter, noting that it was relatively depleted (i.e., has lower values) in ^{13}C relative to carbonate rock (Nier and Gulbransen, 1939; Murphey and Nier, 1941). Further research (Urey, 1947; Wickman, 1952; Craig, 1953; Craig, 1954) related these differences in carbon isotopic ratios to chemical processes involved in photosynthesis. By 1957 standardisation of the techniques for comparing carbon isotopic ratios was achieved, thus providing the benchmark for contemporary investigations (Craig, 1957). The potential for using carbon isotopic geochemistry became more widespread during the 1960s, and included many more investigations on plants (Oana and Deevey, 1960; Stuiver and Deevey, 1962; Parker, 1964; Sackett, *et al.*, 1965; Hall, 1967; Emery *et al.*, 1967). A major breakthrough occurred in 1968, with the discovery that systematic differences in the resultant isotopic ratios of particular plant species were related to different photosynthetic pathways (Bender, 1968).

Since the late 1960s the use of carbon isotope geochemistry has expanded widely, to reconstruct global, regional and local processes, over long and short term timescales. Examining the $\delta^{13}C$ ratios of marine sediments, (e.g., Shackleton, 1977; Bird *et al.*, 1994; Raymo *et al.*, 1997; Zachos *et al.*, 2001) particularly using foraminifera, has facilitated a better understanding of longer term geological processes (Maslin and Swann, 2005). For example, a large negative shift in $\delta^{13}C$ at the end of the Palaeocene (*c.* 55Ma) has been attributed to benthic extinction (Zachos *et al.*, 2001), and less negative $\delta^{13}C$ values during the mid-Miocene (14-16 Ma) is associated with a climatic optimum (Pagani *et al.*, 1999). Pagani *et al.* (1999) found that towards the end of the Miocene the changes in $\delta^{13}C$ can be related to the expansion of C_4 grasses, while the transition from the Miocene to the Pliocene (ca. 5.5 Ma) is associated with further global vegetation change (Cerling *et al.*, 1997). In the more recent past a small positive shift (around 0.15 - 0.7‰) in $\delta^{13}C$ is associated with a shift from glacial to Holocene conditions, due to the expansion of terrestrial vegetation and the retreat of ice sheets (Shackleton, 1977; Duplessey *et al.*, 1984; Berger and Vincent, 1986; Curry *et al.*, 1988; Broeker and Peng, 1993; Maslin *et al.*, 1995). Shifts in the atmospheric carbon dioxide concentrations and associated $\delta^{13}C$ are preserved in ice core records (Friedli *et al.*, 1986; Leuenberger *et al.*, 1992; Francey *et al.*, 1999), and have been tied into global environmental processes.

Speleothems also preserve carbon within the carbonate rock, and the $\delta^{13}C$ can be used to help validate climate models, and provide information about the long term soil CO_2 isotope ratios (Hendy, 1971; Salomons and Mook, 1986). Carbonate rocks have also been used to reconstruct global processes such as monsoon intensity (Fontugne and Duplessey, 1986; Zong *et al.*, 2006).

More recently the use of carbon isotope geochemistry has opened up to more wide-ranging disciplines. Archaeological investigations have been particularly interested in the potential for $\delta^{13}C$ in bone material of humans and other animals to reconstruct environmental conditions (e.g., Heaton *et al.*, 1986; Wu *et al.*, 2007). Hedges *et al.* (2004) studied the carbon isotope ratio of bone material from horse, cattle and deer for the last 40,000 years. They found that each showed a decrease in $\delta^{13}C$ by some 1-2‰ at the transition into the Holocene, and linked this change to the change in

atmospheric CO_2 concentration. Other studies involving carbonate material from animals have shown that it may be possible to track their migration patterns and diets (Cerling *et al.*, 2006).

Palaeoenvironmental studies have also examined the source of organic material in depositional investigations as differences in the $\delta^{13}C$ and C/N ratios of organic material have been linked to differences in sediment provenance (e.g., Fry and Sherr, 1984; Thornton and McManus, 1994; Middelburg *et al.*, 1997; Byrne *et al.*, 2001; Sampei and Matsumoto, 2001). It is this variation that is exploited in the research presented here.

The use of $\delta^{13}C$ and C/N has been shown to be wide ranging, but have often been used for palaeoenvironmental studies. Directly or indirectly they have been used to reconstruct temperature, precipitation, and salinity on local, regional and global scales, and have been used on a wide variety of materials including peat, carbonate rock, bone and ice.

2.4 Understanding carbon isotope geochemistry and C/N ratios in plants

Since the research presented here is primarily concerned with comparing the carbon isotope ratios of bulk peat material to the pollen record, it is most important to understand the processes influencing changes in isotope ratios, and to place this research within the context of previous literature.

2.4.1 What is photosynthesis?

Photosynthesis is the processes by which short wave radiation (400-740 nm) from the Sun is used to drive a number of chemical reactions, which lead to the fixation of carbon dioxide into carbohydrates (Smith and Smith, 2001). This can be expressed as:

$$6CO_2 + 12H_2O \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O \qquad \text{[Equation 2]}$$

Plants can be categorised into C_3, C_4 and CAM plants, and each have differing photosynthetic pathways. For C_3 plants the process of photosynthetic pathways can

be separated into what are commonly known as the light and dark reactions. The light reaction refers to the initial trapping of light energy within the chloroplasts of the leaf. In the dark reaction (so named as it no longer requires sunlight) CO_2 from the atmosphere enters the leaf through openings known as stomata, and is fixed using the enzyme ribulose biphosphate carboxylase oxygenase (rubisco) within the mesophyll cells (Smith and Smith, 2001). The light energy then catalyses the reaction between carbon dioxide and water to form glucose, which is then incorporated into the plant material.

This C_3 photosynthetic pathway is relatively inefficient, since oxygen enters the leaf with carbon dioxide, and is in direct competition with CO_2 for the enzyme rubisco (Farquhar *et al.*, 1980). This means that the rate of uptake of CO_2 is slower than it could be. C_4 plants have developed a different physiological leaf structure to C_3 plants, and have a mechanism which reduces the rubisco competition for CO_2. Although C_4 plants are not found in the fossil record of the Romney Marsh peat, they do occur in some contemporary environments, so this is an important consideration, especially if using modern plant materials to 'calibrate' sediment archives.

The final group of plants are known as CAM plants, using the crassulacean acid metabolism pathway. These plants use a pathway that is effectively a combination of both the C_3 and C_4 pathways (Deines, 1980). CAM plants are typically found in areas of high temperatures and water scarcity, which would lead to high rates of transpiration (Smith and Smith, 2001).

2.4.2 Fractionation of carbon isotopes in plants

Fractionation is the process by which isotopes are preferentially taken up and used in chemical reactions, and occurs within plants as a result of photosynthesis. C_3, C_4 and CAM plants all have different net fractionation rates due to the different enzymes used in the carbon fixation. These plants have adapted to have physiological differences in their leaf structure, as well as behavioural differences, which are best suited to their environment. These adaptations influence the way in which carbon is taken up, fixed and stored within the plant, which has a resultant effect on the fractionation rate of carbon. Fractionation of carbon isotopes from atmospheric CO_2

to eventually become plant material occurs in a two-step process (Deines, 1980). The first stage involves the preferential uptake of the lighter ^{12}C into the leaf itself, through stomata. The amount of fractionation appears to remain relatively constant (McCarroll and Loader, 2006) at around –4‰ (O'Leary, 1980). Theoretically though, environmental stresses will have a knock-on effect to the degree of fractionation. Any stress which leads to the closure of stomata, or lowering of the stomatal density, will lessen the amount of carbon available inside the leaf for carbon fixation. The second stage relates to the preferential uptake of ^{12}C by the carbon-dioxide receptors, such as RUBP and PEP. The net fractionation of C_3 and C_4 plants therefore vary, with C_3 plants having a net fractionation of about 21‰ (Keeley and Sandquist, 1992), and C_4 plants around 6‰ (Smith and Epstein, 1971; Peterson and Fry, 1987). CAM plants usually have a net fractionation between that of a C_3 and C_4 plant. When examining the isotopic ratio of organic matter it is the net fractionation which should form the focus of the investigation, since this most closely relates to the environmental stresses on the plant, rather than using the overall $\delta^{13}C$ value of the organic material (O'Leary *et al.*, 1992).

2.4.3 Carbon/Nitrogen ratios in plants

Total organic carbon (TOC) and total nitrogen (TN) ratios are expressed as the weight ratio in a given sample (Lamb *et al.*, 2006). %TOC/TN is commonly simplified to C/N. One common use for C/N is with environmental reconstructions, where organic material has been preserved. Examples of these include provenancing of organic material in lake sediments (Meyers and Ishiwatari, 1993; Meyers, 1994; Meyers *et al.*, 1995; Meyers and Teranes, 2001; Leng and Marshall, 2004; Lamb *et al.*, 2004); bogs (Barber *et al.*, 2003; Hughes, *et al.*, 2000; Hughes and Barber, 2004); as well as coastal sediments (Fichez *et al.*, 1993; Thornton and McManus, 1994; Schultz and Calder, 1976; Silliman *et al.*, 1996; Middelburg and Nieuwenhuize, 1998; Andrews *et al.*, 2000; Graham *et al.*, 2001; Wilson *et al.*, 2005a; b; Allen *et al.*, 2007). C/N ratios have also been used in other environmental reconstructions, to determine past salinities (Chmura and Aharon, 1995; Muller and Voss, 1999; Yamamuro, 2000; Muller, 2001; Byrne *et al.*, 2001; Westman and Hedenstrom, 2002; Mackie *et al.*, 2005) and long term climatic patterns (Van Geel *et al.*, 1996; Zong *et al.*, 2006).

The reason that C/N ratios can provide so much information about environmental conditions is due to the nature of the sediment preserved. For example aquatic-derived vegetation have C/N usually around 4-10, while terrestrially derived vegetation have C/N usually above 20 (Meyers, 1994). This is because terrestrial plants are lignin and cellulose rich (which is N poor, therefore C/N is higher), while aquatic plants are protein rich (which is N rich, therefore C/N is lower) (Meyers and Teranes, 2001). Theoretically, therefore, the C/N can help to determine not only the amount of organic material (TOC) and thus its derivation (aquatic or terrestrial), but potentially also the plant material type (e.g., wood, leaf, stem components) as each type will have different proportions of carbon and nitrogen. C/N ratios are particularly useful when used alongside $\delta^{13}C$ since some organic matter which have very similar carbon isotope ratios (such as terrestrial C_3 plants and freshwater phytoplankton) have very different C/N ratios (Tyson, 1995).

Coastal studies have often focused on estuaries to examine the relationship between the C/N ratio and the influence of marine conditions, and thus to salinity. Thornton and McManus (1994) found that in the Tay Estuary (Scotland) C/N in the upper estuary was 10-20, while in the lower estuary it was only 10. Similar results have been found by Middelburg and Nieuwenhuize (1998) with C/N of 8-12 at the mouth and 14-21 upstream, and by Andrews *et al.* (2000) in the Humber Estuary and Wilson *et al.* (2005) in the Mersey Estuary, where consistent differences were found between supra-tidal and estuarine sediments. Zong *et al.* (2006) also found that there was a consistent decrease in C/N as distance from the shore increases, representing the decreasing influence of freshwater (and so terrestrially derived organic matter).

2.5 Potential problems and limitations of $\delta^{13}C$ and C/N ratios

In broad terms the influences upon the final ratios (both $\delta^{13}C$ and C/N) of a particular sample can be split into three main categories: the source of carbon which the plant uses; the rate and efficiency of uptake of carbon isotopes by the plant; and the preservation of these carbon isotopes upon decay. It should be noted that these processes are not completely independent of each other, but the separation will help to determine which processes are the predominant ones in a theoretical context.

2.5.1 Source of carbon

The vast majority of carbon available to terrestrial plants comes in the form of atmospheric CO_2. The source of atmospheric CO_2 has not remained constant over time, due to climatic and anthropogenic causes. The termination of the Last Glacial Maximum was associated with temperature amelioration and higher atmospheric CO_2 concentrations (e.g., Jasper and Hayes, 1990; Krishnamurthy and Epstein, 1990; Marino *et al.*, 1992; Turney *et al.*, 1997; Sigman and Boyle, 2000), and the release of the lighter ^{12}C into the atmosphere. A $\delta^{13}C$ shift of around 0.3‰ ± 0.2‰ in ice bubbles has been observed in Antarctic ice core records for the transition into the Holocene (Leuenberger *et al.*, 1992). Through the mid-Holocene period atmospheric $\delta^{13}C$ has remained relatively stable, and it has only been since the Industrial Revolution that the isotopic composition of the atmosphere has significantly changed.

Francey *et al.* (1999) calculated the $\delta^{13}C$ ratio of atmospheric pre 1850 to be –6.4‰. This has been shown to have decreased since the Industrial Revolution (Keeling, 1979; Keeling 1980; Keeling 1995). According to McCarroll and Loader (2006) the atmospheric isotopic ratio has declined by as much as 1.7‰ since 1850, in two separate phases, with a slow decline from 1850 to 1961 of 0.0044‰ annually, increasing to 0.0281‰ from 1962 to 1980, with a similar rate to present. Table G1 (see appendix G) provides a reasonable estimate for the change in atmospheric $\delta^{13}C$ since 1850 (McCarroll and Loader, 2004). The correction values must therefore be applied to all contemporary samples so that comparison of the isotopic values is representative of the plant material rather than the source carbon.

As well as the regional effects of changes in atmospheric $\delta^{13}C$, it is thought that there can be variations on the local scale. For example it has been shown that CO_2 is 'recycled' in enclosed environments, such as woods and forests, because the normal turbulent mixing of gases is incomplete. This is also known as the 'canopy effect' (Vogel, 1978). Kondo *et al.* (2005), in an experiment in Japan, found a near 2‰ reduction in $\delta^{13}C$ in the ground and field layers compared to the lower and upper canopies, since the CO_2 concentrations were much lower at the base of the canopy.

This has been linked to the 'juvenile effect' where trees which are younger appear to have anomalously low $\delta^{13}C$ relative to the overall forest (Schleser and Jayasekera, 1985). Although it is not thought that younger trees have different isotope ratios to more established trees, the fact that the trees are not as tall means that they are using recycled CO_2 found in the lower canopy.

Problems associated with the source of carbon are further complicated by the underlying geology. As an example, carbonate minerals have less negative carbon isotopic ratios compared to coal and the original plant material. Furthermore, any stored water in the rock will contain dissolved carbon, usually either as carbon dioxide or methane, which may be isotopically different to that of the overlying soil (Darling *et al.*, 2005). To reduce errors associated with non-contemporaneous carbon being sampled, the laboratory process must be rigorous to only sample the organic matter in question. Geology could also have indirect influences on the carbon isotope and C/N ratios by influencing water availability and acidity of the soil. Each of these influence plant growth and potentially could become limiting environmental stress factors.

2.5.2 Environmental stresses

Local, regional and global climatic changes can affect the way in which plants develop by limiting the photosynthetic capacity of a plant. The two most obvious changes in climate which can affect a plant are precipitation and temperature. Favourable conditions can lead to greater biomass production, with some species becoming more abundant, while others become less so. Alterations in vegetation composition in the fossil record have been used in the past to show climatic changes (e.g. Shackleton, 1977; Duplessey *et al.*, 1984; Berger and Vincent, 1986; Curry *et al.*, 1988; Broeker and Peng, 1993; Maslin *et al.*, 1995). One objective of this is study is to test the hypothesis that large changes in precipitation and temperature could have the effect of changing the carbon isotope signature of deposited organic material. This could occur by different vegetation compositions leading to different carbon isotopic signatures. It could also occur by preferential uptake of the heavier ^{13}C by the photosynthetic enzymes in stressed conditions, leading to higher (less negative) $\delta^{13}C$.

Studies investigating the effects of temperature and water availability on the carbon isotopic signature of plants are scarce, but those undertaken indicate that significant changes in the isotopic record can occur. Temperature increases can lead to increased transpiration, and thus plants respond by closure of stomata (see below) (Llorens *et al.*, 2004). This means that there is less CO_2 diffusion into the leaf, and so less carbon is available for carboxylation (Brugnoli and Bjorkman, 1992), which can in turn lead to less negative $\delta^{13}C$ (Farquhar *et al.*, 1989). Elevation in temperature also has the effect of increasing the decomposition rate of organic material, at least initially, which leads to nitrogen being lost in the original plant material, thus leading to higher C/N (Berg and Meentemeyer, 2002).

In certain environments, such as raised bog and alder carr, having the necessary water availability is crucial to sustaining the vegetation community. Drought conditions can lead to water stresses upon the plant, which can have the effect of lowering the net photosynthetic capacity (Brugnoli and Bjorkman, 1992). The effect of precipitation on the carbon isotope ratios has been explored with mixed results (Miller *et al.*, 2001; Warren *et al.*, 2001; Van de Water *et al.*, 2002; Llorens *et al.*, 2004). The real consideration is the availability of water to the plant, which is not necessarily proportional to the amount of precipitation. Other factors influence the water availability including temperature, storage capacity of the soil, when the precipitation falls, and in what form.

When investigating coastal and estuarine environments, a major consideration must be the effects of salinity on the vegetation community. It is known that salinity affects the carbon isotope signatures of individual plants (Bowman et al., 1989; Sandquist and Ehleringer, 1995; Twiddy, 1996; Poss *et al.*, 2000; Mackie *et al.*, 2005; Choi *et al.*, 2005) and forms the basis of many estuarine reconstructions (Emery *et al.*, 1967; Schultz and Calder, 1976; Chmura and Aharon, 1995; Middelburg and Nieuwenhuize, 1998; Mackie, 2004; Malamud-Roam and Ingram, 2004; Choi *et al.*, 2005). In the Schelde Estuary (Belgium) the differences in $\delta^{13}C$ and C/N between the upper and lower estuaries become very apparent (Middelburg and Nieuwenhuize, 1998). In the upper estuary the $\delta^{13}C$ and C/N were –26.9‰ and

17.0 respectively, whereas closer to the marine source the $\delta^{13}C$ increased to −23.5‰, and the C/N ratio decreased to 10.3. This can be explained by the increase in marine derived organic and inorganic material which have less negative $\delta^{13}C$ and more nitrogen in the lower estuary, and also the impact of salinity stresses on plants causing stomata to close and thereby increasing $\delta^{13}C$.

The above potential stresses on a plant are often interlinked within a system, and it can be very difficult to distinguish between the variables. Other factors, such as nitrogen availability (Condon *et al.,* 1992) and altitude (Morecroft and Woodward, 1990; Körner *et al.*, 1991; Menot and Burns, 2001; Treydte *et al.*, 2001) will also influence the carbon isotope and C/N ratios of the plant and peat material, but are also influenced by water availability and temperature.

One of the main ways in which a plant can control the effects of environmental stresses is through their stomata. The conductance (i.e., the rate of diffusion) across the cuticle of the leaf itself is very low, and therefore gas diffuses through the stomata (Kersteins, 1996), and the overall rate of diffusion into the mesophyllous cells within the leaf is dependent upon the stomatal density and stomatal size (Woodward, 1986; Woodward, 1987; Woodward and Bazzaz, 1988). Furthermore developing epidermal cells in leaf have the potential for differentiating into stomata, and are able to do this in times of climate amelioration, or when there are fewer environmental stresses upon the plant. Under high CO_2 concentrations, it is a selective advantage to have a lower stomatal density as this reduces water loss. This has been shown to occur in a number of C_3 plants (Madsen, 1973; O'Leary and Knecht, 1981; Thomas and Harvey, 1983), and in fact it has been suggested that, according to laboratory experiments, up to 90% of the differences in final carbon isotope ratios of plant material within a species may be due to changes in atmospheric concentration (Arens *et al.*, 2000; Beerling and Chaloner, 1993). Woodward (1986; 1987) and Woodward and Bazzazz, (1988) have shown that herbaceous plants, grasses and trees have consistently reduced their stomatal density as a result of recent increases in CO_2 concentrations. It has been shown, however, that plants do not always reduce their stomatal density under increased CO_2 concentrations. For example C_4 plants have been shown not to significantly change

their stomatal density in relation to environmental stresses or atmospheric CO_2 change (Royer, 2001), whilst Eide and Birks (2006) found that *Betula pubescens* and *Pinus sylvestris* did not show any proportional relationship between the stomatal density and CO_2 concentrations. Taking this into account, changes in $\delta^{13}C$ of fossil material could tentatively be used as indicators of past atmospheric CO_2 concentrations, and environmental stresses upon the plant.

2.5.3 Post-depositional processes

The carbon isotope and C/N ratio of plant material is not always fully represented in the peat record due to post-depositional processes. Perhaps the main problem in any sedimentological study to consider is erosion and resedimentation. This is of particular importance when considering coastal environments which are naturally dynamic systems. Of the environments to be explored in this study, saltmarsh is prone to loss of material out of the system due to its proximity to the coast. Saltmarshes are also traps for fine-grained clastic sediment and reworked organic material. Howarth (1993) found that most saltmarsh material is lost upon death due to transportation along tidal creeks to the sea. These tidal creeks will also have the impact of redepositing material, thus making it more difficult to discern the autochthonous and allochthonous plant material in fossil saltmarsh deposits.

Decomposition is the process whereby nutrients in the senescent litter are released into the soil, and become available to microbes and can be re-used in plant growth. The remaining un-decomposed material becomes part of the soil organic matter (Vivanco and Austin, 2006) and forms the basis of sedimentological studies. The chemical alteration of soil from initial deposition to the 'final' fossil product is known as diagenesis. Diagenetic alteration in relation to carbon isotope and C/N ratios have been explored by a number of authors (e.g., Benner *et al.*, 1987; Ember *et al.*, 1987; Meyers, 1994; Aerts *et al.*, 2001; Wilson *et al.*, 2005a; Lamb *et al.*, 2006). The amount of alteration can be variable, leading to a $\delta^{13}C$ decrease of around 2‰ (Hayes *et al.*, 1989) to 4‰ (Chmura *et al.*, 1987). This could be a significant difference when investigating terrestrial peat where $\delta^{13}C$ differences between different vegetation communities are so small. The reason for the reduction in bulk organic $\delta^{13}C$ is the change in molecular composition of plants. The vast majority of

terrestrial plant material is made of lignin, cellulose and hemi-cellulose. Lignin is relatively depleted in ^{13}C (more negative $\delta^{13}C$) compared to cellulose and hemi-cellulose, and is more resilient to decay (Benner *et al.*, 1984a; Fogel *et al.*, 1989). Selective decomposition of the more labile compounds of cellulose and hemi-cellulose will therefore lead to a more negative $\delta^{13}C$ ratio compared to the whole plant material. Some plants within a vegetation community may be more resistant to decay, which means that they could be better represented in the fossil record (Deines, 1980). This in turn could lead to differences in both $\delta^{13}C$ and C/N.

Compounds in plants not only have differing $\delta^{13}C$, but also have different C/N. The selective loss of material will therefore lead to changes in the C/N ratios relative to the original plant material. Small changes in the %C and %N can lead to large changes in the C/N ratio of a sample (Sampei and Matsumoto, 2001) which means that diagentic alteration is a big concern in studying fossil deposits. Distinguishing between marine and terrestrial environments should however still be possible. Terrestrial environments contain much more lignin and cellulose (which is nitrogen poor) than a marine environment, and so the initial C/N is much higher. The limitation may therefore exist within the terrestrial vegetation communities, where the initial C/N are roughly equivalent.

As well as micro-faunal activity, bacterial action is a principal way in which organic material is broken down. Bacterial action increases the nitrogen content of soil which decreases the C/N (Rice and Hanson, 1984) increasing the availability for plant growth (Valiela *et al.*, 1985). Bacteria also use ^{12}C preferentially to ^{13}C (Kaplan and Rittenberg, 1964; Benner *et al.*, 1987; Coffin *et al.*, 1989) leading to more negative $\delta^{13}C$. The rate of decomposition increases as temperature and water availability becomes more favourable. This means that changes in $\delta^{13}C$ and C/N could theoretically be used to determine local and regional environmental conditions.

Temporal variations in carbon isotope and C/N ratios change have been investigated for a wide variety of plant types (Benner *et al.*, 1987; Alberts *et al.*, 1988; Jahren, 2004). They have been shown to vary over the annual cycle, due to the changing source of nitrogen through the year (Switsur *et al.*, 1994). Following senescence of

plant material during winter nitrogen becomes available with the onset of spring and summer, and therefore can become incorporated (White and Howes, 1994). This is of particular importance when comparing the contemporary and fossil C/N.

2.7 Conclusions

This chapter has provided a theoretical framework for the use of carbon isotope geochemistry and C/N ratios in environmental reconstructions. It has explored the development of the science since the 1960s before focusing on more recent applications. It has shown that the science can be applied to the use in vegetation reconstruction, but there are a number of limitations which need to be fully considered, before robust conclusions can be made. The following chapter introduces applies this knowledge to the study sites investigated in this research.

Chapter 3: Site descriptions

3.1 Introduction

This chapter begins by introducing the study region for this investigation, together with a rationale for its selection. It explores the vegetation communities found within the fossil record, before providing explanation for the selection of similar contemporary sites within the area. It also identifies limitations for each of the investigated sites, and thus introduces similar investigations from across the UK to supplement this research. Finally the primary vegetation communities which are investigated are explored in the context of stable carbon isotopic geochemistry and C/N.

3.2 The Romney Marsh study area

Romney and Walland Marshes are situated in south-eastern England and together with Denge Marsh and the surrounding valleys constitute the Romney Marsh depositional complex (Figure 3.1). It covers an area 27,000 ha and thus makes it the third largest reclaimed marshland in Britain (Waller *et al.*, 1999; Evans *et al.*, 2001). One of the main reasons for this site being chosen to assess the applicability of a new proxy technique is due to the extensive studies which have already been completed in the area. It has been the focus of archaeological, vegetational, sea-level and climatic investigations (Eddison and Green, 1988; Eddison, 1995; Eddison *et al.*, 1998; Long *et al.*, 2002).

Historically the depositional complex has been the focus for sea-level research for over 150 years. Early reconstructions have mainly used litho-stratigraphical and relative dating techniques (Elliott, 1847; Drew, 1864; Burrows, 1884; Lewis, 1932; Lewis and Balchin, 1940), before the use of radiocarbon dating had been discovered. The interest in the site has been maintained in more recent times. Coastal wetlands preserve a large volume of carbon (Cannell *et al*, 1993; Milne and Brown, 1997; Bauer and Druffel, 1998; Henman and Poulter, 2008) and therefore the long-term stability of the area is an important concern. This is especially important with issues such as rising rates of sea-level.

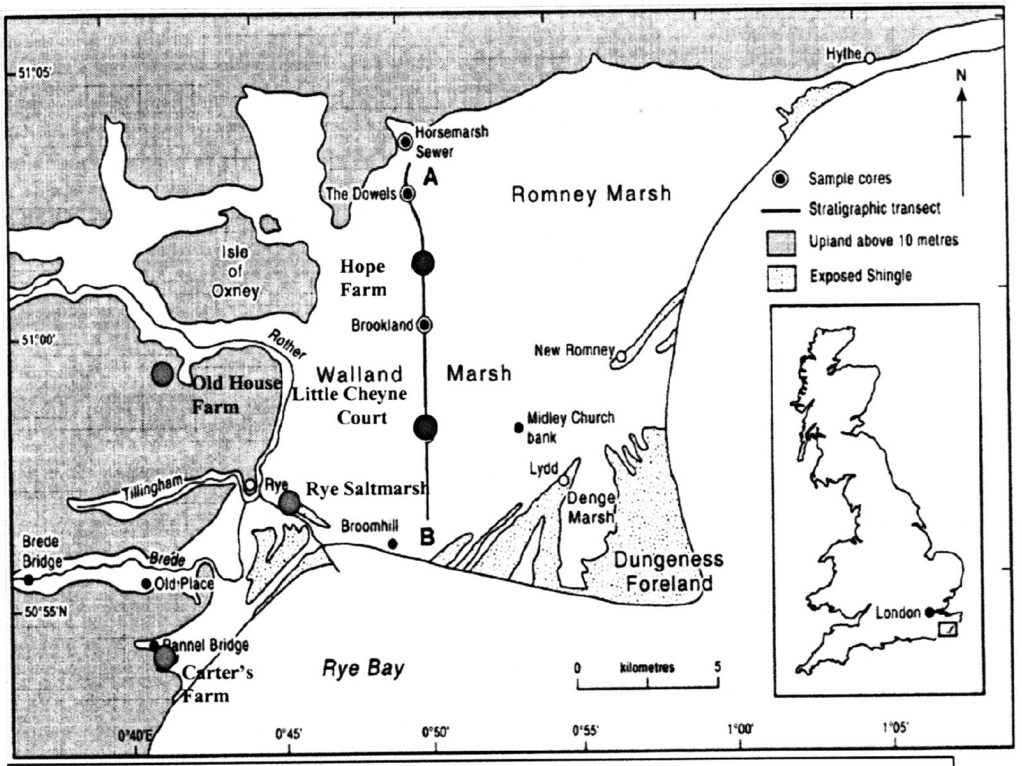


Figure 3.1: *Map showing the Waller* et al. *(1999) transect (A-B) across the Romney and Walland Marshes. The locations of the cores (in green) and contemporary sites (in red) investigated are also shown. Note the Brede, Tillingham and Rother Valleys to the west of the Romney, Walland and Denge Marshes (adapted from Waller* et al., (1999)).

The use of multi-proxy techniques have been utilised to reconstruct the morphodynamics of the Romney Marsh depositional complex, and these include litho-stratigraphy (Waller *et al.,* 1988; Long and Innes, 1995; Long *et al.,* 1996; Dix *et al.*, 1998; Spencer *et al.,* 1988; Long *et al.,* 1998; Evans, *et al.,* 2001); palynology (Waller, 1993; Waller, 1994; Long and Innes, 1995; Waller *et al.,* 1999; Waller, 2002, Waller and Kirby, 2002); diatoms (Long and Innes, 1995; Evans *et al.*, 2001); and foraminifera (Evans *et al.*, 2001; Evans and Kirby, 2002; Waller, 1994). These various techniques have aided a thorough dated reconstruction of the coastal morphodynamics of the Romney Marsh depositional complex through the Holocene. Much of the radiocarbon dated peat material from the region also yields a stable carbon isotopic value, which can then be included as part of this investigation.

Green (1968) identified four main general litho-stratigraphic units in the area above bedrock; sand; blue clay; main marsh peat; and younger alluvium. Of these units, the

main marsh peat, which forms the focus of this research, has been found to be laterally persistent across the marsh (Waller *et al.,* 1988; Long and Innes, 1995; Long *et al.*, 1998; Waller *et al.*, 1999), with thicknesses usually around two metres across the main marsh, but even thicker in the western valleys. Radiocarbon dates on the main marsh peat suggest the peat spread in an easterly direction, from the westerly valleys of Brede, Tillingham and Rother (Waller, 1993), in the lee of a prograding gravel barrier that developed across Rye Bay towards Hythe. Peat accumulation is also thicker towards the north of the marsh (backmarsh sites), furthest away from the coast (Long and Innes, 1995). Eventually barrier breakdown, from ca. 2000 yr BP, a result of reduced sediment supply, increased storm activity, and reduced rate of sea level rise caused tidal inlets at Hythe and New Romney (and eventually Rye) to form (Long and Hughes, 1995), bringing about an end to peat forming communities.

3.3 The core records

Waller *et al.* (1999) studied a transect of cores from across the Romney Marsh depositional complex, examining the development of coastal vegetation during peat formation (Figure 3.1). Across the marsh there was a clear distinction between northerly and southerly marsh sites in terms of their vegetation succession patterns (Figure 3.2). In the north, such as at Horsemarsh Sewer and Brookland, minerotrophic communities, mainly alder-dominated carr replaced saltmarsh and fen communities until the end of peat development, whereas in the more southern sites, such as Little Cheyne Court, ombrotrophic communities, notably ombrotrophic bog, replaced the saltmarsh and poor fen communities for much of the record. To capture a diversity of vegetation communities I have selected two cores from Hope Farm and Little Cheyne Court for analysis. The peat from Hope Farm contains saltmarsh, fen, alder-dominated carr, sedge fen and *Myrica gale*-dominated communities; whilst the peat at Little Cheyne Court contains saltmarsh, poor fen, bog, and sedge fen communities. Therefore seven vegetation communities are available for study. The main communities however are alder carr from Hope Farm and bog from Little Cheyne Court, with cyperaceae being present in both cores. Saltmarsh will also be investigated since it is the first main peat forming community in all cores in the Waller *et al.* (1999) study.

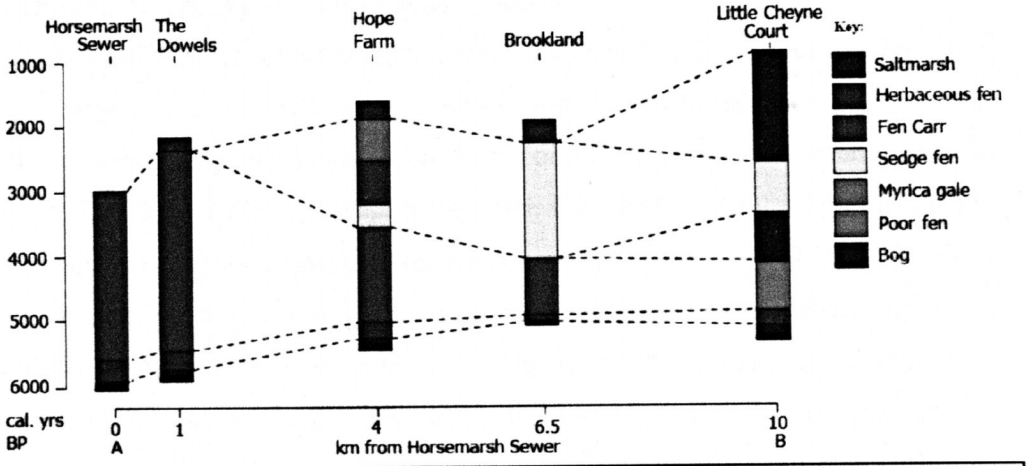


Figure 3.2: *Dominant vegetation communities from the Romney Marsh main peat layer based on pollen analysis (adapted from Waller* et al. *(1999)).*

Between them they form the bulk of the peat material and are influenced by local climatic and environmental stresses which may be picked up in the $\delta^{13}C$ and C/N records. Therefore, four vegetation communities will form the basis of this research; alder carr, saltmarsh, bog and sedge fen.

For a full investigation into the use of stable carbon isotope geochemistry and C/N ratios this research needs to be placed into a local and regional context. Although there are very few investigations directly examining the $\delta^{13}C$ and C/N ratios of vegetation communities, data are usually available as part of the verification process in calculating radiocarbon dates. The extensive research from the Romney Marsh area has generated radiocarbon dates for many of the vegetation communities (e.g., Waller, 1994; Long *et al.*, 1998; Waller *et al.*, 1999; Schofield and Waller, 2005; Waller *et al.*, 2006), which also have $\delta^{13}C$ data, and information about the vegetation community that is being dated. These data will be used alongside data from other ombrotophic bog (e.g., Charman *et al.*, 1999; Chiverrell, 2001; Hughes and Barber, 2004; Caseldine and Gearey, 2005; Langdon *et al.*, 2005), saltmarsh, (e.g., Wilson, 2004; Wilson *et al.*, 2005; Andrews *et al.*, 2000; Allen *et al.*, 2007), alder carr (Andrews *et al.*, 2000; de la Vega Leinert *et al.*, 2000) and sedge fen (de la Vega Leinert *et al.*, 2000; Anderson, 2002) communities from elsewhere in the UK to supplement this research and help provide more robust conclusions.

3.4 The contemporary vegetation communities

To understand the processes operating in the fossil core records from Hope Farm and Little Cheyne Court it is necessary to understand the processes which are operating in the contemporary environment. In terms of the modern day formation of the Romney Marsh depositional complex, there are some key differences from that of the past, mainly due to anthropogenic influences. Much of the wetland in the Romney Marsh region has been reclaimed for agricultural purposes. As a result many of the vegetation communities which once existed, as shown in the fossil record, simply do not exist in the area any longer (e.g., Ferry and Waters, 1979). Two communities do remain though, a small area of saltmarsh, south-east of Rye, and two alder carr woodlands, at Carter's Farm and Old House Farm. Data collected from these three sites will therefore form the basis for the comparison to the fossil record. The site descriptions for each follow.

3.4.1 Carter's Farm

Carter's Farm is situated near Pett, in East Sussex (Figures 3.1; 3.3). It contains a small area (approximately 120 m x 40 m) of species poor alder-dominated carr woodland, with *Alnus glutinosa* by far the most dominant species within the upper canopy, often 100% (See Appendix A: Table A4). This means that it is particularly useful in comparison to parts of the fossil core with high *Alnus* pollen counts. A lower canopy is absent from much of the area. However, where present *Alnus glutinosa, Sambucus nigrum* and *Salix cinerea* are the dominant species. The field and ground layers were variable dependent upon the elevation above the woodland stream which provides much of the water to the woodland. In the wettest areas, *Carex pendula, Mentha aquatica, Geranium robertianum, Sphagnum* spp., as well as unidentified *Orchidaceae* were commonly found. On the higher (and drier) ground species such as *Ranunculus repens,* were found. Species such as *Urtica dioica, Rubus fruticosus, Lonicera periclymenum, Valeriana dioica* and *Dryopteris dilatata* were found throughout the woodland.

3.4.2 Old House Farm

Old House Farm is located within the parish of Peasmarsh, East Sussex (Figures 3.1; 3.4). The area investigated is known as Willow Beds, and is an area of woodland dominated by *Salix cinerea* and *Salix fragilis* (See Appendix A: Table A3). Alongside the woodland stream that forms one edge of the outer boundary of the woodland are *Alnus glutinosa trees*, and these form a dominant part of the lower canopy. The reason for the selection of this site was to compare the nature of fen carr environments within two similar climatic and geological regimes. With the domination of *Salix* spp. within the upper canopy it serves as a useful comparison to any *Salix* dominated alder carr environments found within the fossil record. The field and ground layers typically consisted of *Urtica dioica, Heracleum sphondylium, Iris pseudacorus, Ranunculus repens* and *Sphagnum* spp., while *Rubus fruticosus, Peucedenum palustre* and *Galium aparine* occur occasionally.

3.4.3 Rye saltmarsh

Rye saltmarsh is situated to the south-east of Rye, between the Rother Estuary and a sea defence bank (Figures 3.1; 3.5). Grazing by sheep and geese on one side of a tidal creek has led to different patterns of vegetation growth. Domination by *Salicornia* spp., *Spergularia marina, Puccinellia martima,* and occasionally *Glaux maritima* and *Honkenya peploides* exists within the grazed section, whereas taller *Aster tripolium, Seriphidium maritimum,* as well as *Suaeda maritima* and *S. verna* exist in the ungrazed section (see Appendix A: Table A5). Within the ungrazed section *Spartina townsendii* (a C4 plant) was locally abundant. With the network of tidal creeks the rest of the saltmarsh may be influenced by dead and decaying *S. townsendii.* The tidal creeks also supply salt water and sediment almost up to the sea defence bank during high tide conditions.

Figure 3.3: *Carter's Farm alder-dominated carr. Note* Alnus glutinosa *in foreground, decending into stream in background.*

Figure 3.4: *Old House Farm alder-dominated carr.* Urtica dioica *is dominant component in foreground, and* Alnus, Salix *form the background.*

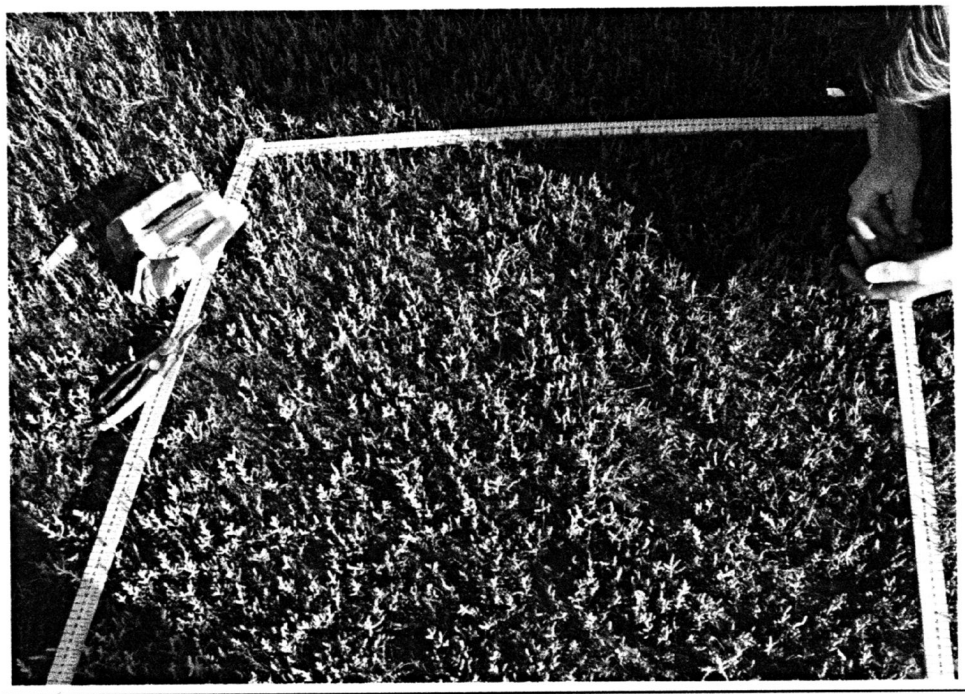


Figure 3.5: *Rye saltmarsh. Showing sampling of* Salicornia *in western grazed section of saltmarsh.*

3.4.4 Other contemporary fieldsites

The alder carr woodlands remaining in the Romney Marsh depositional complex are localised, and the stands are of a small area. This means that comparison to the alder carr found in the fossil cores the contemporary communities may not be fully representative since fewer species are found in the contemporary alder carr environments than fossil ones. For this reason, two more comparable far-field sites were also selected for sampling, Wheatfen and Calthorpe (Figure 3.6). The sites are situated in Norfolk and have been selected for two reasons. First, average annual precipitation and temperature of Romney Marsh and Norfolk are relatively similar and secondly the contemporary ecology of the sites have already been investigated in detail (Waller *et al.*, 2005; Binney *et al.*, 2005). The main likely difference between the sites which could manifest themselves in different carbon isotopic ratios is the geology on which the vegetation is being supported. In Norfolk the geology is chalk, whereas in Romney Marsh it is Wealden clay, and this may affect the storage of groundwater, as well as changing the isotopic composition of the groundwater itself.

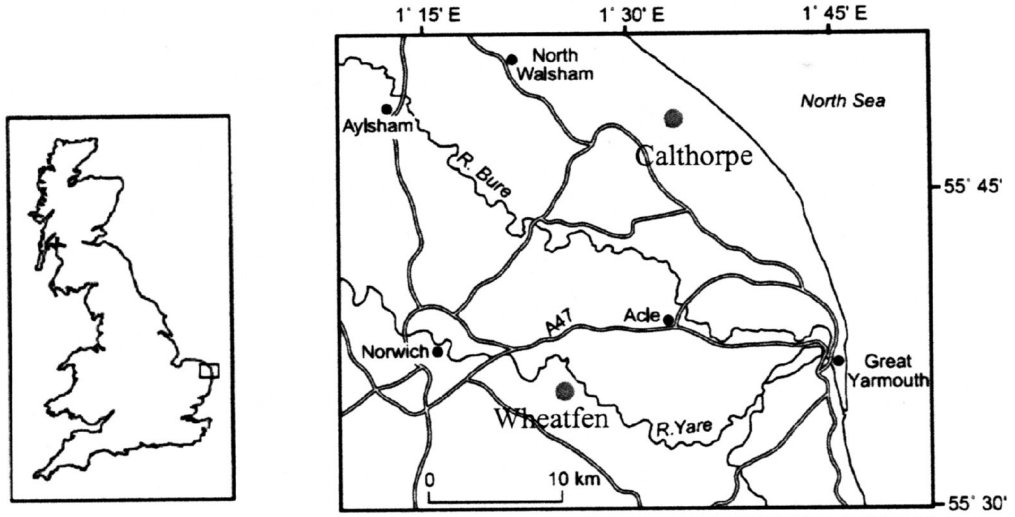


Figure 3.6: *Location of Calthorpe and Wheatfen alder-dominated carr woodlands found in Norfolk.*

3.4.5 Calthorpe

Calthorpe is situated some 25 km north-east of Norwich, and is an English Nature Reserve (Figures 3.6; 3.7). The reserve is an area of woodland surrounding a reedswamp, which itself envelopes an area of open water. The carr is generally dominated by *Alnus glutinosa, Salix cinerea* and *Betula pubescens* both in the upper and lower canopy (see Appendix A: Table A1). The field and ground layers are species rich, (although less so than Wheatfen) with common occurrence of *Dryopteris dilatata, Rubus fruticosus, Lonicera periclymenum* and *Thelypteris palustris,* and often areas of *Sphagnum* growth. From Waller *et al.* (2005) *Mentha aquatica, Carex paniculata,* and other plant species usually found in alder carr settings, have also been recorded.

3.4.6 Wheatfen

Wheatfen reserve is situated to the south-east of Norwich, just south of the River Yare, forms part of the Ted Ellis Nature Reserve (Figures 3.6; 3.8). The reserve covers a range of wetland habitats, maintained by water from the River Yare, and a series of dykes. The tidal influence of the nature reserve makes the site especially useful in comparison to the Romney Marsh Holocene vegetation communities.

Figure 3.7: *Calthorpe alder-dominated carr. Note* Dryopteris dilatata, Phragmites australis, Quercus robur *in the foreground.*

Figure 3.8: *Wheatfen alder-dominated carr with* Ribes present in the field layer.

The main area for investigation in this project is that of 'Surlingham Wood' and 'The Carr', and forms part of the area investigated by Waller *et al.* (2005). Although *Alnus glutinosa* does not dominate the upper or lower canopies, it forms a major part of it, up to 40% in some subsites (see Appendix A: Table A2). Alder carr species such as *Rubus fruticosus, Cirsium palustre, Salix cinerea, Urtica dioica, Ribes rubrum, R. nigrum, R. uva-crispa* and *Dryopteris dilatata* are often present. Vegetation data in Waller *et al.* (2005), and from the warden David Nobbs (Appendix B) show that *Filipedula ulmaria, Galium palustre, Mentha aquatica* are also commonly found within the fen carr. These species, according to Rodwell (1991a), are species which are expected to be found within alder carr woodlands.

3.5 Description of vegetation communities investigated

Interpreting the $\delta^{13}C$ and C/N data from Hope Farm and Little Cheyne Court will require an understanding of the main vegetation communities investigated. This section defines each of the communities, offers explanation for their evolution and successional patterns, and provides examples where these communities have been used in carbon isotopic studies.

3.5.1 Alder-dominated fen carr woodland

Alder-dominated fen carr is an important community in the main marsh peat, but defining an alder carr woodland has proven to be problematic in both contemporary and historical contexts. Woodlands themselves do not tend to be spatially uniform in their structure, and are related to local hygroclimatic, and geological demands (Rodwell, 1991a). Furthermore woodlands are variable in a temporal context, due to processes such as autogenic succession, competition from other plant species, and the changing hygroclimatic and thermoclimatic regimes (Kazda, 1995). Although there are very few investigations examining the $\delta^{13}C$ and C/N of alder carr communities (Mackie, 2004; Andrews *et al.*, 2000), historically there have been many investigations to determine the composition and evolution of this vegetation community (McVean, 1956a; b; Tallantire, 1992; Waller *et al.*, 2005), and the way this could relate to palaeoenvironmental investigations.

Tallantire (1992) has reviewed the spread of Alder [*Alnus glutinosa* (L.) Gaertn.] into the British Isles using numerous radiocarbon dated peats and macrofossils from across the UK. Tallantire has assumed that the spread of alder is represented in the pollen record by an increased abundance from 3% to above 10%. This increase signifies that alder was likely to have been growing *in situ*. Ideally there should be alder macrofossils preserved in the peat, and the percentage of *Alnus* would be well above the 10% value, but this serves as a minimum requirement for an alder carr environment. *Alnus glutinosa* is a high pollen producer (Andersen, 1970; Bradshaw, 1981; Sugita *et al.*, 1999), and therefore is likely to be over-represented in the pollen record. Equally important is the fact that *Alnus* pollen is representative not only of the autochthonous source of alder trees, but also of the regional and local alder vegetation (Sugita, 1994; Calcote, 1995; Bunting *et al.*, 2004). As a result Huntley and Birks (1983) interpret *Alnus*-dominated vegetation in Holocene studies as requiring >25% TLP, and this value is much more preferable.

Investigating the contemporary environments has allowed sub categorisation of alder carr woodlands (Rodwell, 1991a). Alongside the obvious requirement for alder to be a constituent of the vegetation community, other plant species are often associated with, and indicative of the environment. These include *Salix cinerea* (Grey Willow); *Salix fragilis* (Crack Willow); *Betula pubescens* (Downy Birch); *Carex paniculata* (Greater Tussock Sedge); *Rubus fruticosus* (Blackberry); *Cirsium palustre* (Marsh Thistle); *Galium palustre* (Common Marsh Bedstraw); *Filipedula ulmaria* (Meadowsweet); *Eupatorium cannabinum* (Hemp-agrimony); *Urtica dioica* (Stinging Nettle); *Dryopteris dilatata* (Common Buckler Fern); *Mentha aquatica* (Water Mint) and *Valeriana officinalis* (Common Valerian) (Rodwell, 1991a).

Alder carr is a transitional vegetation community (Walker, 1970), which should succeed into bog communities. However, alder carr often persists for hundreds of years (Waller, 1993; Waller, 1994; Mighall and Chambers, 1995; Long and Innes, 1995; Waller *et al.*, 1999). For alder carr to be sustained in the long term, it must have a constant water supply. McVean, (1953) stated that regeneration would be possible under waterlogged conditions, but would require a rising water table at the same rate as which sediment is being produced. The mechanism proposed is due to a

slow rate of sea-level rise, allowing internal degeneration and re-establishment of the alder carr (Kidson and Heyworth, 1973; Smyth and Morgan, 1989; Waller, 1993).

Alder is thought to have spread into the UK via the south-east of England (Bennett and Birks, 1990; Tallantire, 1992) up to 8300 cal yr BP, and spread northwards and westwards over the next millennium. Tallantire (1992) proposed that the initial slow spread of alder from south-east England, dated to *c.* 7800-7500 cal yrs BP, was due to drier conditions and cooler temperatures. Although the impact of the Boreal chronozone cannot be investigated in this study (since peat formation at Hope Farm began *c.* 5500 cal yrs BP), it will be possible to investigate the impact of wetter and cooler periods upon the alder carr stable carbon isotopic composition.

The impact of increased salinity on the stable isotopic ratios of alder carr sediments can also be investigated with the Hope Farm peat layer, since at the top of the core there is a return to mudflat-like conditions, due to marine inundation. It is known that water salinity above 5‰ leads to root formation failure (Ericson, 1972), in turn leading to the collapse of the vegetation community.

3.5.2 Ombrotrophic bog

Ombrotrophic bogs in north-west Europe have already been shown to be sensitive to climatic changes (e.g., van Geel *et al.*, 1996; Chapman and Shackleton, 2000; Mauquoy and Barber, 2002; Mauquoy *et al.*, 2002; Barber *et al*, 2003; Hughes and Barber, 2003; Pancost *et al.*, 2003), especially in relation to wet and dry shifts, due to switches from oceanic to continental climate regimes, related to the North Atlantic thermohaline circulation. Carbon isotope geochemistry could serve as a way of testing these previous theories, and also explore the applicability of their use in reconstructing palaeo-precipitation in ombrotrophic environments.

Sphagnum is generally a genus that occupies wetland habitats, and this forms a major constituent of ombrotrophic bogs (Daniels and Eddy, 1985; Aerts *et al.*, 2001). The process by which *Sphagna* acquire and lose their water and carbon dioxide needed for photosynthesis differs from that of higher plants. In higher plants water is brought from the roots, via the xylem into the leaves, where it can be used for photosynthesis,

or may be lost through evapo-transpiration via stomata. *Sphagna* do not possess any stomata, and thus has an alternative mechanism with which water is obtained and lost. Water moves through cell walls through osmosis, and into specialist cells, known as hyaline cells. This means that it is not always necessary for the moss to be in contact with the water table for there to be sufficient water for photosynthesis, since precipitation falling directly on the moss can be used (Schipperges and Rydin, 1998). *Sphagna* are able to cope with short-term water shortages (Gupta, 1977; Proctor, 1982), since the hyaline cells effectively provide a water reserve, however long-term water shortages will lead to desiccation of the plant material, and eventually to death of the plant (Schipperges and Rydin, 1998). There is a clear contrast to other vegetation communities where water availability is crucial to sustaining the environment. In ombrotrophic bogs, precipitation is a very important factor in controlling growth, whereas other environments, such as alder carr can use precipitation, run off as well as groundwater stores for their water supply (Barber and Charman, 2003). Short-term changes in the water table in ombrotrophic bogs will not necessarily lead to changes in the abundance of *Sphagnum*, but may change the rate of photosynthesis, and thus in turn the carbon isotopic signatures of the resultant plant material. Local moisture conditions are likely to impact on *Sphagna*, and can lead to spatial variability of the moss (Price *et al.*, 1997). This in turn can lead to differences in both $\delta^{13}C$ and C/N of the plant material and deposited organic material.

To fully evaluate the use of stable carbon isotope geochemistry in this environment, the ombrotrophic bog material of Little Cheyne Court must be presented in relation to data collected from the ombrotrophic bog communities of the UK., and also the nearby Netherlands, Belgium and Germany, as climatic influences on the south-east of England are likely to be seen in north-west Europe as a whole.

3.5.3 Saltmarsh

Saltmarshes are one of the most intensively studied of vegetation communities in relation to carbon isotope geochemistry (e.g., Chmura and Aharon, 1995; Andrews *et al.*, 2000; Malamud-Roam and Ingram, 2001; Wilson *et al.*, 2005a, b) since marine sediments are easily distinguishable from more terrestrial sediments, and thus

provides a good proxy for palaeo-salinity. Due to the relatively harsh environmental conditions caused by tidally driven changes in salinity in saltmarshes there are a range of adaptations plants have made to survive. One of these adaptations is the photosynthetic pathways that the plants have evolved. In saltmarshes all three photosynthetic pathways exist, and in general reflect changes in salinity, with C_3 plants being the most terrestrial; C_4 are the most marine; and CAM plants form and intermediate group (Deines, 1980). C_4 plants have much less negative $\delta^{13}C$ than C_3 plants which enable marine and terrestrial plants to be more easily distinguished (DeLaune, 1986; Peterson and Fry, 1987; Cloern *et al.*, 2002). Unfortunately this technique has limited applicability in Holocene investigations in north-western Europe since most C_4 plants have been introduced, such as *Spartina alterniflora* during the nineteenth century (Rackham, 1986), while *Spartina townsendii* is of more recent origin. Comparison between the modern day and fossil plant assemblages are therefore complicated by the prevalence of *Spartina townsendii* in the modern saltmarsh community at Rye. Laboratory tests have concluded that *S. townsendii* has a photosynthetic pathway similar to C_4 plants (Thomas and Long, 1978), and so plant material will have less negative $\delta^{13}C$.

A further complication with saltmarsh sediments is due to allochthonous material being deposited caused by tidal processes. The roots and stems of saltmarsh material also serve to block the return path of sediment to the sea (Leonard and Luther, 1995), which means that marine algae and other marine aquatic plants will be deposited alongside the autochthonous material, leading to less negative $\delta^{13}C$. To make matters worse the majority of saltmarsh biomass is lost at the end of the growing season, through degradation or exportation (Howarth, 1993), which means that the sediment is less representative of the original vegetation cover.

While these various processes may result in less negative sediment $\delta^{13}C$ than would be expected based on the plant material itself, it does have the advantage of distinguishing marine and terrestrial environments. Similar studies from the Mersey Estuary (Wilson *et al.*, 2005a; b), the Humber Estuary (Andrews *et al.*, 2000) and the Severn Estuary (Allen *et al.*, 2007) will serve as useful comparisons of saltmarsh

carbon isotopic ratios to that of the Rye Saltmarsh sediment, as well as the fossil material from Hope Farm and Little Cheyne Court.

3.5.4 Sedge fen

Sedge fen communities are found in both the Hope Farm and Little Cheyne Court cores (Waller *et al.*, 1999). There are however great difficulties in defining a sedge fen community, due to its high degree of variability. In the case of Hope Farm it indicates the reduction of tree species, replaced by an increase in Cyperaceae and Poaceae, thus a more open habitat. In the case of Little Cheyne Court the sedge fen vegetation community, although having similar Cyperaceae and Poaceae percentage abundances the nature of the vegetation community is very different. Increases in Cyperaceae abundance here indicate the drying of the acidophilus community as *Sphagna* is gradually replaced. Clearly the Hope Farm Cyperaceae community will have a much higher woody component than the Little Cheyne Court Cyperaceae community, which in turn could lead to different $\delta^{13}C$ values, and certainly to different C/N values within the fossil record.

3.6 Conclusions

This chapter has rationalised the selection of Romney Marsh as a study area, as it has been extensively and thoroughly investigated in the past. It focuses on two cores from the Waller *et al.* (1999) transect, and examines the vegetation communities found within them. It explains how the fossil core vegetation communities have been selected for examination, and how similar contemporary vegetation communities from nearby locations are chosen. Finally the chapter provides a definition of each of the communities, and other investigations which have used carbon isotopic geochemistry and C/N ratios. The following chapter reveals the methodological approaches for the sampling of the contemporary and fossil environments outlined in this chapter.

Chapter 4: Methodological approaches

4.1 Introduction

This chapter details the sampling strategy of the contemporary and fossil vegetation communities, together with the advantages and limitations of the techniques involved. The process of laboratory analysis of the samples is also described.

4.2 Contemporary data

The sampling strategy for alder carr and saltmarsh followed where possible the strategies described in Rodwell (1991a; b) respectively. Sampling collection was undertaken in September 2006 for the following reasons. Firstly, some of the plant species were still flowering or were fruiting, and most still had their leaves, thus aiding identification. Secondly, with the onset of autumn, many of the leaves (and in some cases twig material) are lost, so collection of this material more closely represents the leaf material as it reaches the ground before decay.

4.2.1 Alder carr woodland sampling

Although the four sites (Calthorpe, Wheatfen, Old House Farm and Carter's Farm) have been described as "alder carr" communities, their nature is actually hugely variable internally, due to a range of factors including water supply, slope angle and local geology. The aim of the sampling strategy, therefore, is to sample this variability while ensuring that the sample area is broadly representative of an alder carr environment, as detailed below.

The alder carr woodland in the Romney Marsh sites was smaller than the Norfolk sites, and so the plot size for investigation needed to be reduced accordingly. The Norfolk sites had a plot size of 25 m x 25 m, whereas the Romney Marsh sites had a size of 15 m x 15 m. In both cases the area was measured and marked out using tape measures and string. Within these quadrats the abundance of species in the upper and lower canopies were estimated on a percentage coverage basis.

From the centre of the main quadrats, four smaller quadrats were measured out (10 m x 10 m), and shrub and field layer species were recorded on an occurrence basis.

Four 1 m x 1 m quadrats, at each corner of the 10 m^2 quadrat, recorded the ground layer species on an occurrence basis. This process can be seen schematically in (Figure 4.1). The centre point of each of the quadrats was recorded using a handheld GPS.

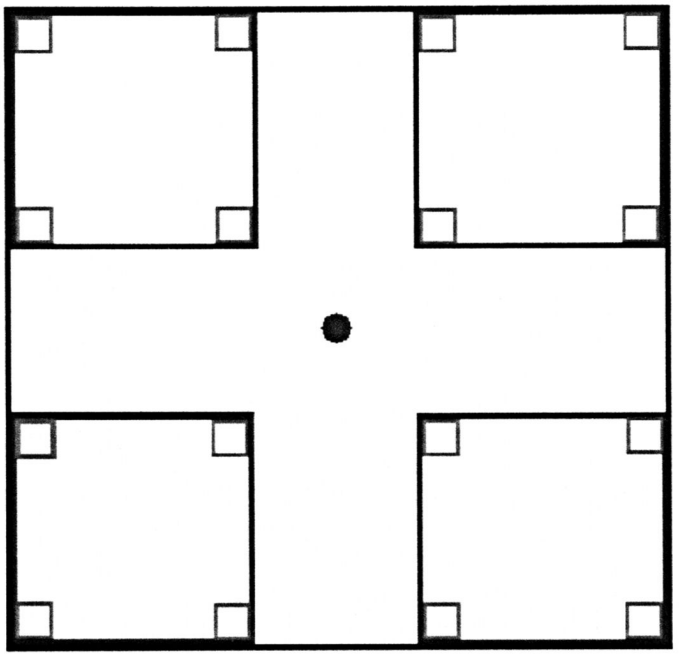


Figure 4.1: *Schematic diagram showing sampling strategy for the alder-dominated carr woodland. The outer black box represents the 25 m x 25 m quadrat. The four blue boxes in each of these corners represents the 10 m x 10 m quadrats in which field and ground layers were surveyed. The sixteen red boxes represent the 1 m x 1 m quadrats in which the ground layers were surveyed. The centre green dot represents the position of the GPS reading.*

The specific location of these sample plots varied between locations and was based on a qualitative decision, dependent upon the sites themselves. For the Romney Marsh sites, since the extent of the alder carr woodland was smaller, the quadrats were marked out in a linear fashion from one edge of the woodland to the other. The Norfolk sites allowed a more rigorous selection process. Sites were selected to capture variability in the abundance of key species, such as *Alnus glutinosa, Salix fragilis* and *Betula pubescens*, in the upper and lower canopy, as this in turn would allow comparison to particular parts of the Hope Farm core. This is viewed as being preferable to a random selection approach since this approach captures not only the 'typical' alder woodland, but also the variation which can be found within it. Maps

showing the sampling sites are shown in Figures 4.2; 4.3; 4.4; and 4.5 (© Crown Copyright/database right 20(yy). An Ordnance Survey/ (Datacentre) supplied service).

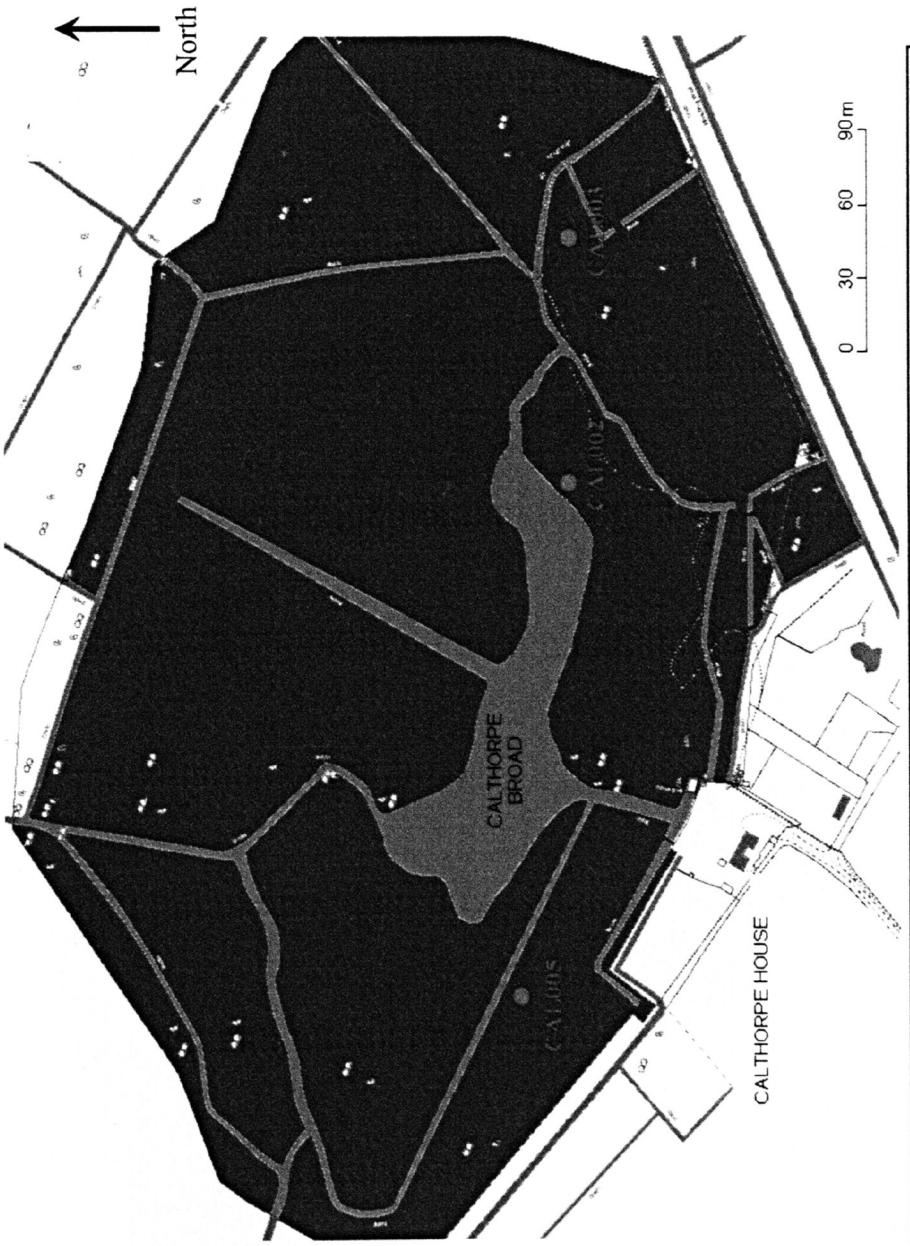


Figure 4.2: *Map of Calthorpe, with locations of the 25 m x 25 m quadrats indicated.* "© Crown Copyright/database right 20(yy). An Ordnance Survey/ (Datacentre) supplied service

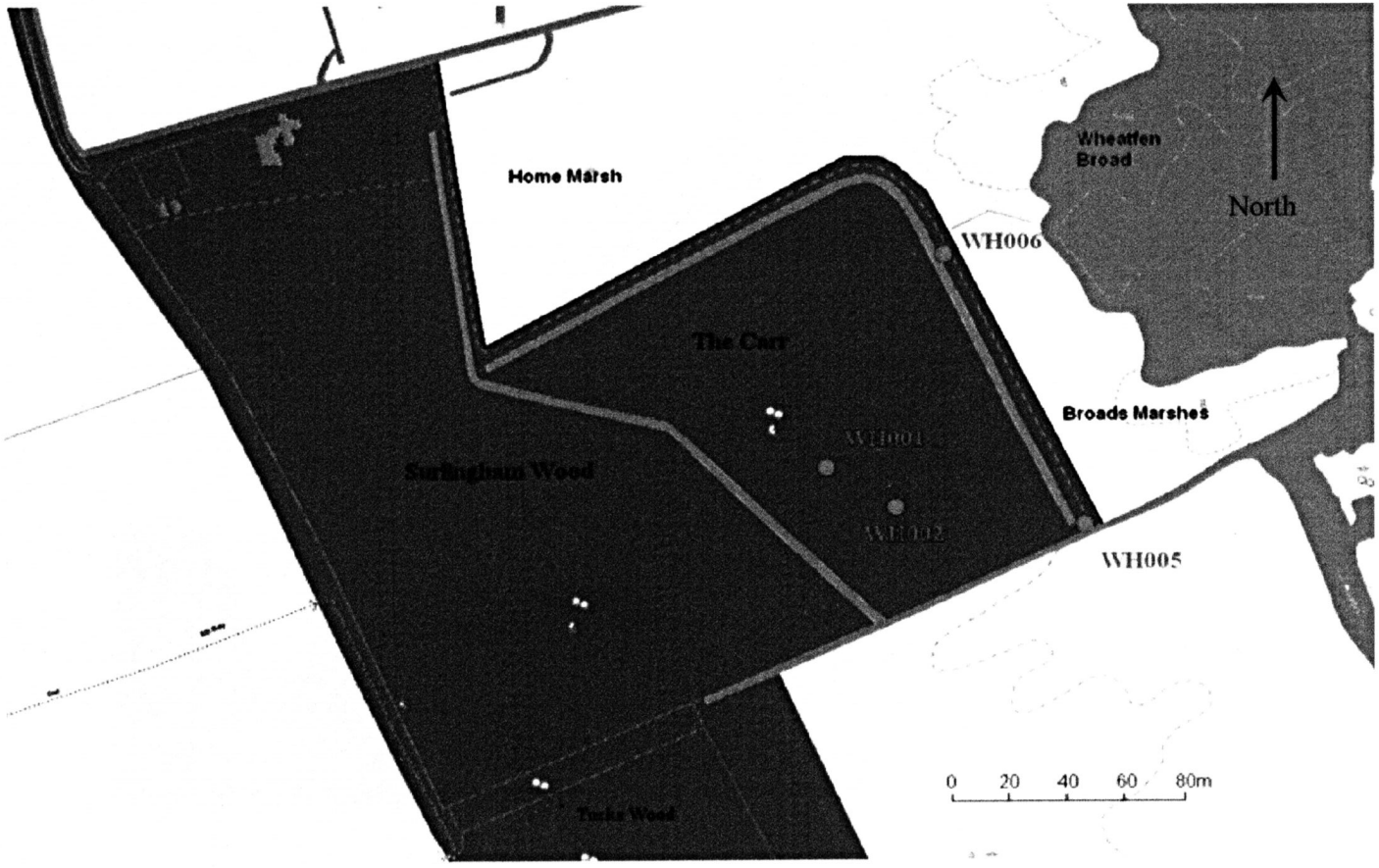


Figure 4.3: *Map of Wheatfen, with locations of the 25 m x 25 m quadrats indicated*

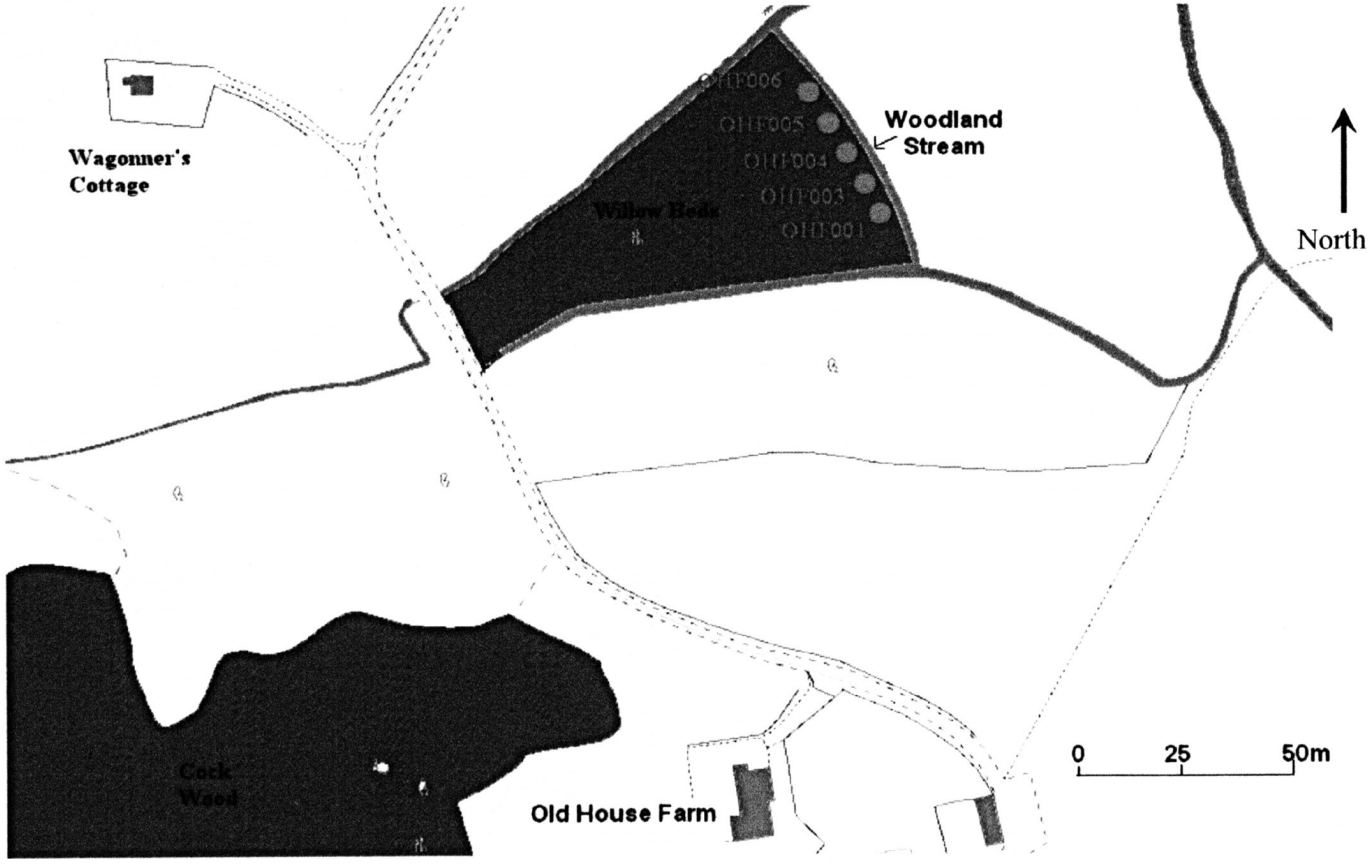


Figure 4.4: *Map of Old House Farm, with locations of the 15 m x 15 m quadrats indicated*

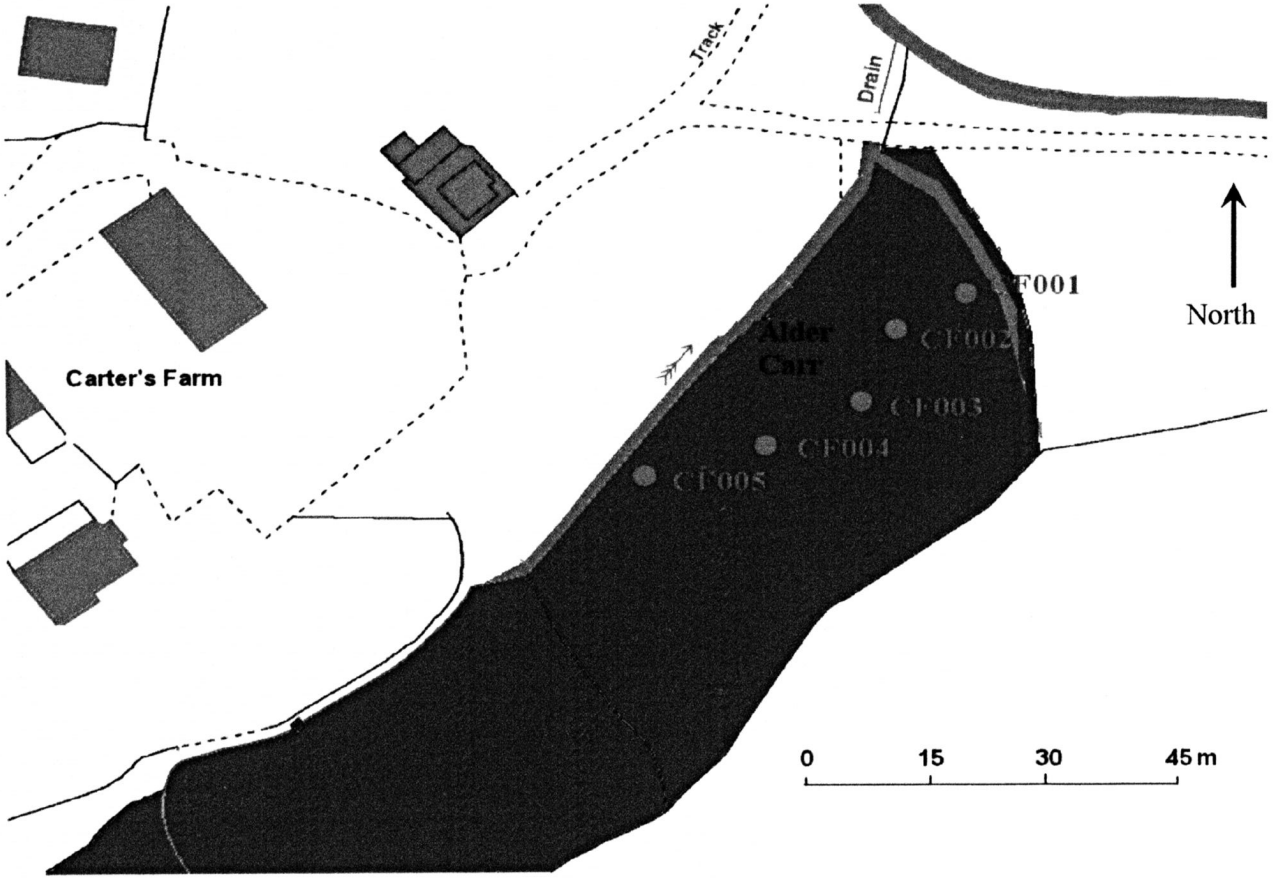


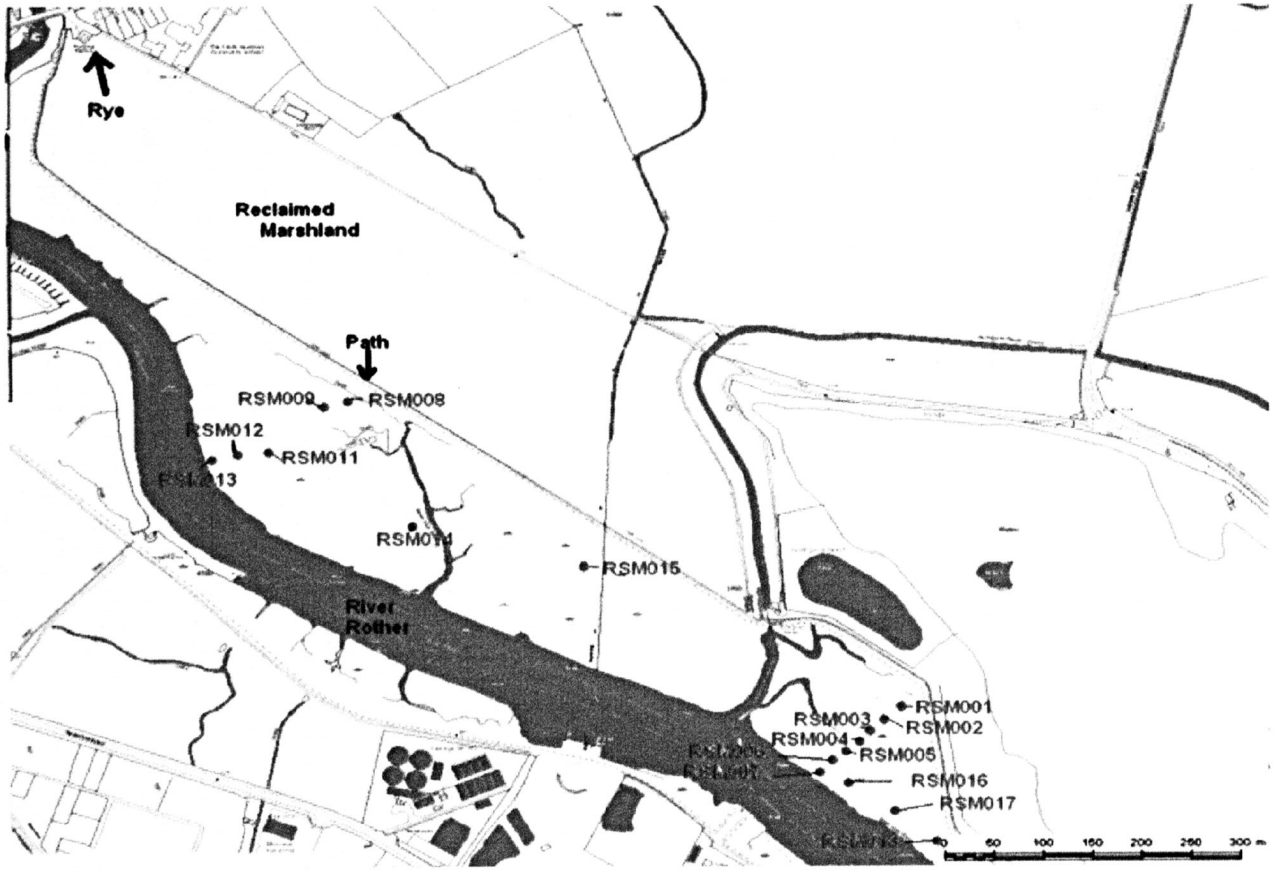
Figure 4.5: *Map of Carter's Farm, with locations of the 25 m x 25 m quadrats indicated*

The biomass of an alder carr woodland can be split simplistically into four main components; the upper canopy, lower canopy, field layer and ground layer. Therefore sampling needed to reflect the different types of plant material that these represented. The different plant materials identified are twig, leaf and root material. Each of these plant material types were collected for dominant and indicative species of alder carr woodlands, as identified by Rodwell (1991a). This material was stored in labelled paper bags, to remove excess moisture. Repeat sampling of plant material within alder carr woodlands was also undertaken to reduce the potential sampling errors. Soil samples were also taken from 3-5 centimetres in depth, to take into account humification processes and labelled and stored in plastic test-tubes. On return to Durham University, all samples were stored in a freezer at $-80^{o}C$.

4.2.2 Saltmarsh sampling

The theoretical frameworks for species selection, plant material selection and sample plot selection are similar to those of the alder carr woodland, although clearly only herb and ground layers occur in the saltmarsh. There are relatively few sites in south-east England where 'pristine' saltmarsh (thus approximating the saltmarsh in the fossil record) is found. In the Romney Marsh depositional complex the only expanse of saltmarsh is at Rye (Figure 4.6 © Crown Copyright/database right 20(yy). An Ordnance Survey/ (Datacentre) supplied service), and therefore this was selected as the environmental and geological conditions are likely to the best approximate to that found in the Holocene peat record of Waller *et al.* (1999).

A tidal creek forms a dividing line between the grazed and ungrazed marshes and is useful in allowing domination of different species of plant. The sampling model followed where possible the guidelines set out by Rodwell (1991b). A total of seventeen 1 m x 1 m quadrats were placed across the marsh with varying degrees of domination of the different plant species. The approximate percentage coverage of each plant was recorded for each quadrat, and a GPS reading taken at each of the sites. These sub-sites were selected on a qualitative basis, to capture as much variability as possible, while being representative of saltmarsh environments found within the Hope Farm and Little Cheyne Court cores.



North

Figure 4.6: *Map of Rye Saltmarsh, with locations of the 1 m x 1 m quadrats indicated*

Twig, leaf and root material of dominant species within the quadrats were sampled, and stored in labelled paper bags to absorb excess moisture and prevent 'sweating'. Soil samples were also taken from 3-5 cm below the surface, and stored in labelled plastic test-tubes. Subsequently this material was stored at −80°C in a freezer in Durham University.

4.3 Potential sampling errors and limitations

Sampling of natural environments inevitably leads to complications, and possible sampling bias. The main limitation to the approach of sampling is the extent to which the approach represents the vegetation community under consideration. For the alder carr, leaf and twig material in much of the upper canopy remains unrepresented, since leaf and twig samples tended to be selected at a maximum height of three metres above ground. The potential effects of this selection could be variations in the source atmospheric carbon due to recycling in the undercanopy (see Section 2.5.1), however these differences are likely to be <1‰ and therefore negligible. Secondly the collection of root samples, although subterraneous, tended to be close to the surface, to minimise damage to the ecosystem, however there could be differences in the carbon isotopic geochemistry of root material due to its position relative to the water table. Thirdly, the soil samples collected were taken as an average sample between 3 and 5 centimetres below the surface, to allow for humification processes, and thus more representative of the plant community as a whole. However, subconsciously large twig samples within the soil layer are likely to have been ignored, though they will form a significant part of the final soil, and so the results need to be considered carefully. The shrub, herb and ground layers were much easier to representatively sample, mainly due to their smaller size and accessibility. In all of the sampling, plant material was taken from a variety of specimens across the sample area, and also from different branches, heights above ground level, parts of the root etc. The reason for this wide-ranging sampling was to provide a more accurate average of the leaf, twig and root components for a particular species within a sample area, and to capture as much variability as possible. This may be seen as a limitation due to possible variation in $\delta^{13}C$ of some plant material (e.g., Kohorn *et al.*, 1994; Twiddy, 1996; Rundgren *et al.*, 2003; Loader and Rundgren, 2006), even from the

same plant, in this case the averaging of plant material is in fact more representative of the final homogenised soil.

Another major consideration for woodlands is the relative contribution of plant components within the system. It is difficult, if not impossible, to accurately quantify the relative biomass of different parts of the woodland, such as trees, herbs and mosses, as well as components such as fungi, microfauna and bacteria. This means that the relationship between the living plant material and the resultant soil material is difficult to understand.

For saltmarsh environments, sampling strategies will have similar limitations to the alder carr sampling. Full representation of the vegetation community is not always possible. The sampling strategy adopted here was designed to capture as much variability between the high and low marsh species, while also representing the Hope Farm and Little Cheyne Court core material. The most important consideration for the Rye saltmarsh is occurrence of *Spartina townsendii. S. townsendii* is a C_4 plant which is dominant across much of the marsh. This plant is not found within the fossil record, and so sample plots with less influence from *Spartina* were therefore preferred.

4.4 Core data

The core data, which the contemporary data is being compared to, were collected from the same cores used in the Waller *et al.* (1999) analysis, and stored in Kingston University. The approach of the project is to have a high-frequency sampling of the Hope Farm and Little Cheyne Court cores, to capture both longer and shorter term climatic changes, and show internal variability within vegetation communities. For this reason 1 cm contiguous sampling was chosen. A 1 cm^3 sample was taken from within the core (i.e., not exposed to external influences) from each of the 1 cm intervals. These were labelled before being stored in a 4°C fridge in Durham University prior to analysis.

4.5 Laboratory processes

The laboratory process can be split into two main parts; the preparation and analysis of the samples for their $\delta^{13}C$ and C/N ratios. Ultimately the sampled plant and soil material needed to be reduced to a representative 1 milligram sample of highly homogenised powder. The process to achieve this is different for the plant and soil material. For the plant material, samples were first stored at $-80^{o}C$ in a freezer in Durham University. Water was then removed by freeze-drying overnight. The root and twig samples had to be cut into small pieces (a few mm^3) so that the process would be completed effectively. These samples were then crushed into smaller pieces, before being thoroughly homogenised. A smaller sub-sample was then taken from this and put in a ball-mill at 350 rpm for 5 minutes (or longer if required). This ensured that the material did not get too hot, as this could liberate CO_2. The powdered material was then re-labelled and stored in vials which had been cleaned with de-ionised water.

The soil material required a different approach, as it contains not only organic carbon but potentially also carbonates, which needed to be removed. A 1 cm^3 sample of soil was placed in a labelled beaker (cleaned with de-ionised water) of at least 50 millilitres of 5% hydrochloric acid (HCl) overnight. The solute was the filtered by Büchner filtration (a vacuum is created to draw the water out of the soil mixture), and repeatedly washed with de-ionised water to remove the HCl. The soil material was then put on labelled watch glasses before being oven-dried at $40^{o}C$ overnight. The dried material was then ball milled at 350 rpm for 3 minutes (or longer if required) before being stored in sterilized vials. Any apparatus used in the above processes, such as the Büchner funnels, watch glasses, beakers and vials, had all been cleaned thoroughly with de-ionised water prior to use and re-use.

The powdered material for plant and soil material were analysed at the Natural Environmental Research Council Isotope Geosciences Laboratory (NERC-NIGL) facility at Keyworth. The samples were weighed using high precision scales (to 1 μg). 1 milligram samples of plant material, and 10 milligram samples of soils were measured in tin capsules (as around 0.5 mg of carbon is required for $\delta^{13}C$ and C/N analysis. The percentage carbon and nitrogen were measured using a Carbo Erba

analyser, and the $\delta^{13}C$ ratios were calculated using a Carbo Erba 1500 on-line to a VG Triple Trap and Optima dual-inlet mass spectrometer. The $\delta^{13}C$ values were calibrated to the VPDB scale, using the laboratory standard (homogenised broccoli). The associated error in the laboratory process is around $\pm$ 0.1‰ for $\delta^{13}C$.

4.6 Summary

This chapter has explored the sampling strategies for the alder carr and saltmarsh contemporary environments, and acknowledged and tried to reduce potential errors and limitations. It has also described the sampling methodology of the core material. It has explained in detail the laboratory methods by which data was collected, and how sources of error were minimised. The following two chapters will explore the contemporary and fossil carbon isotope and C/N ratios of the sampled vegetation and cores.

Chapter 5: Results from the contemporary environment

5.1 Introduction

The contemporary sampling from Romney Marsh and Norfolk has the potential to provide useful information about the relative contributions of certain species and plant material types in the formation of organic deposits, specifically in relation to the investigated Romney Marsh cores. This chapter analyses contemporary $\delta^{13}C$ and C/N of the investigated alder carr and saltmarsh plants and soils. In particular it attempts to understand the processes leading to the soil $\delta^{13}C$ and C/N ratios, in relation to geology, precipitation, and the original plant material.

5.2 Alder-dominated carr

The sampling strategy employed in the alder carr woodlands of Romney Marsh and Norfolk Broads has allowed different process which may be influencing the final soil $\delta^{13}C$ and C/N to be studied and identified. The differences between the Romney Marsh and Norfolk data in part highlight differences in the climatic and geological controls on the $\delta^{13}C$ and C/N of the soils (Section 2.5.1). No two alder-dominated carr environments are identical. Therefore $\delta^{13}C$ differences of plant material within vegetation communities highlight the relative contribution of certain plant species to the final soil $\delta^{13}C$. $\delta^{13}C$ of contemporary plant material and soil samples have been 'corrected' to pre-Industrial levels, using the table of McCarroll and Loader (2004) (Section 2.5.1) to enable comparisons to the Holocene deposited material. Soil samples are assumed to represent contemporary soils. However, since samples have been taken from 3-5 cms below surface level (to create an averaging effect of the vegetation community) it is likely that these samples are in fact older.

5.2.1 Alder-dominated carr in Romney Marsh

The two investigated alder carr woodlands in Romney Marsh are Carter's Farm (Figure 3.3) and Old House Farm (Figure 3.4). Data from the Meteorological Office, UK shows that for the nearest nearby 'Wye' Station, the precipitation for these sites from 1970-2000 is 775 mm per year.

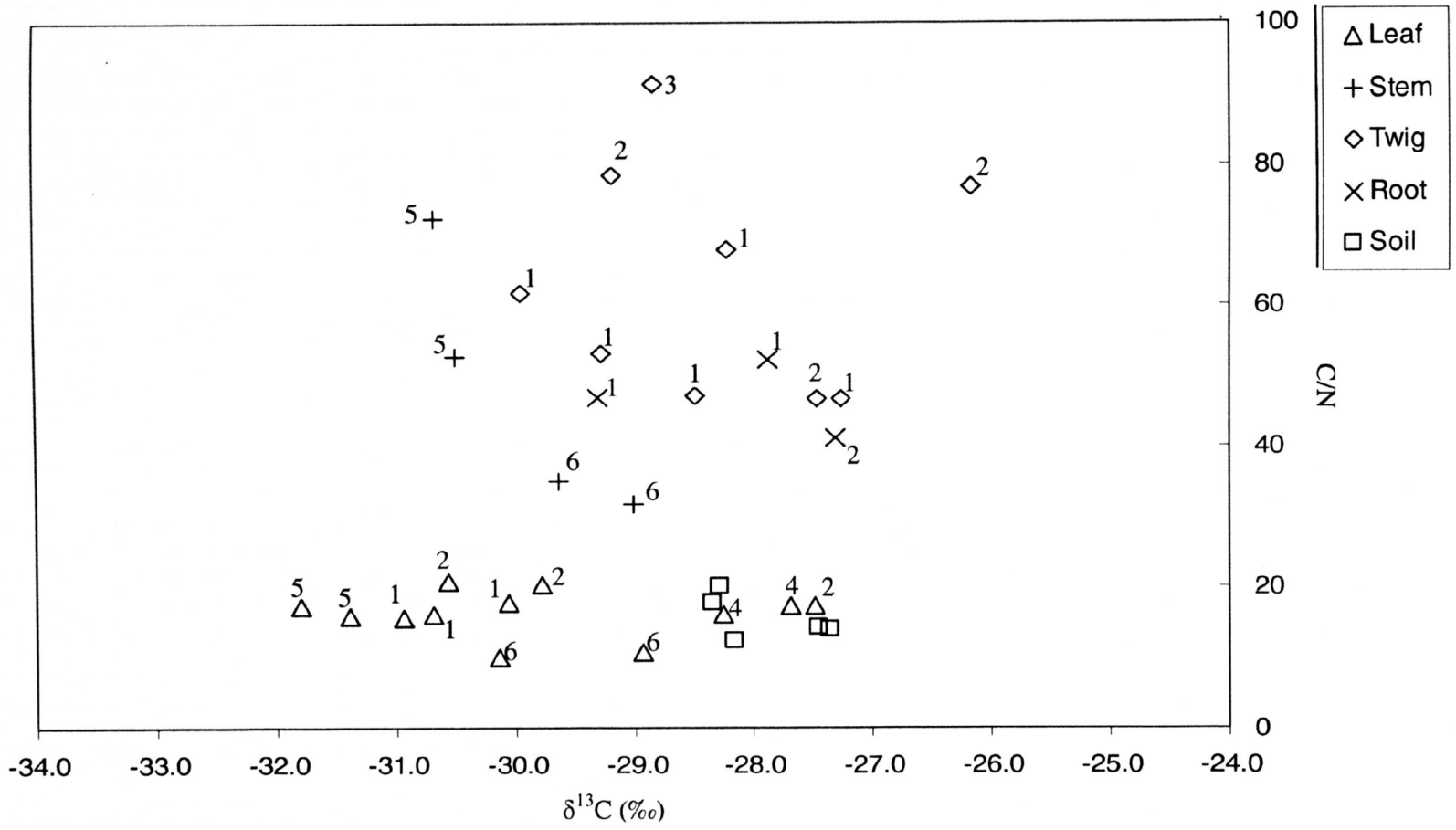


Figure 5.1: *Carter's Farm $\delta^{13}C$ and C/N for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species.. (1)* Alnus glutinosa *(2)* Salix spp. *(3)* Betula spp. *(4)* Dryopteris dilatata *(5)* Rubus fruticosa *(6)* Urtica dioica.

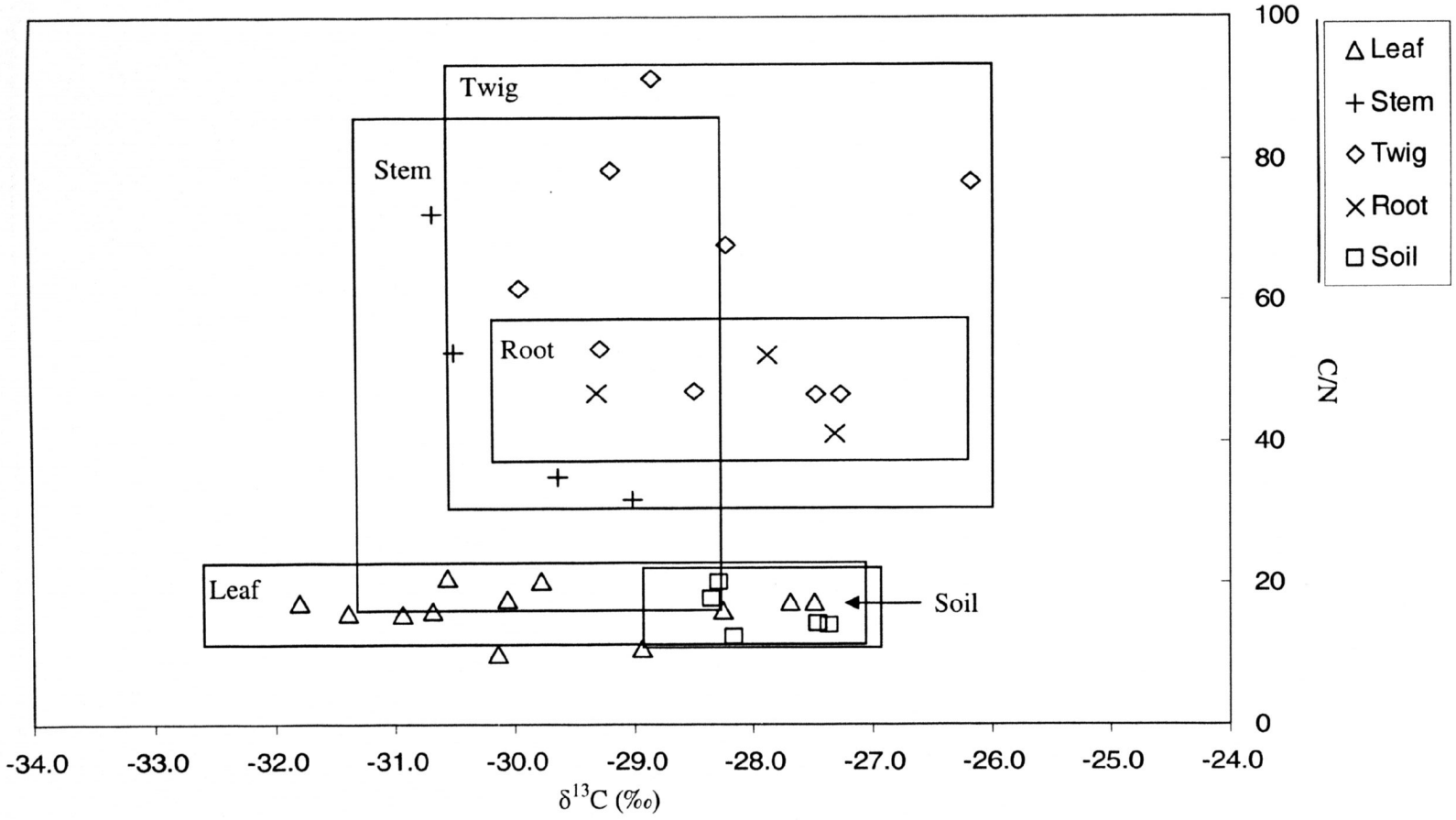


Figure 5.2: *Carter's Farm $\delta^{13}C$ and C/N for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species. Boxes indicate the mean ± 2 x standard deviations for each of the material types, showing variability within the data.*

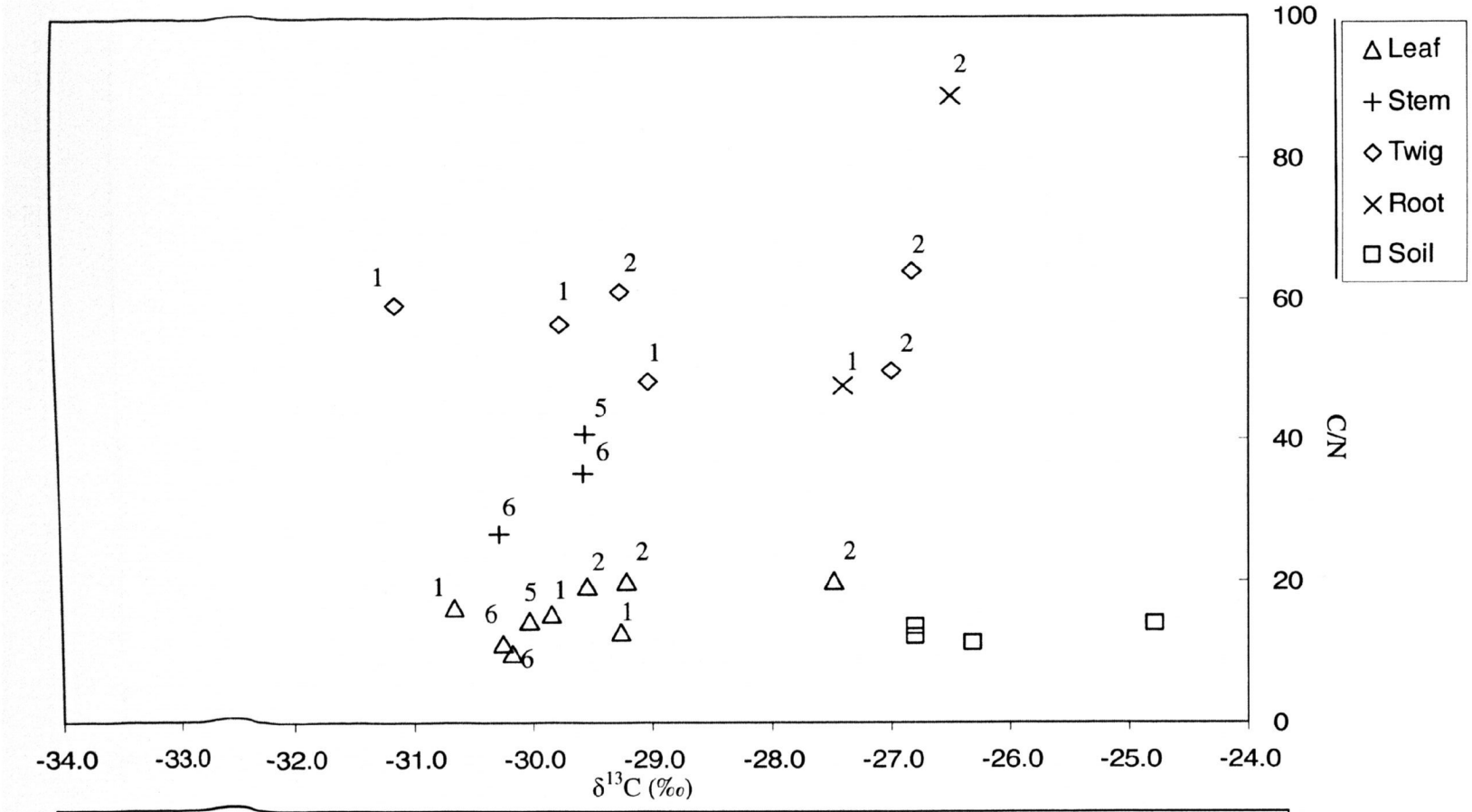


Figure 5.3: *Old House Farm $\delta^{13}C$ and C/N for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species.. (1)* Alnus glutinosa *(2)* Salix spp. *(3)* Betula spp. *(4)* Dryopteris dilatata *(5)* Rubus fruticosa *(6)* Urtica dioica.

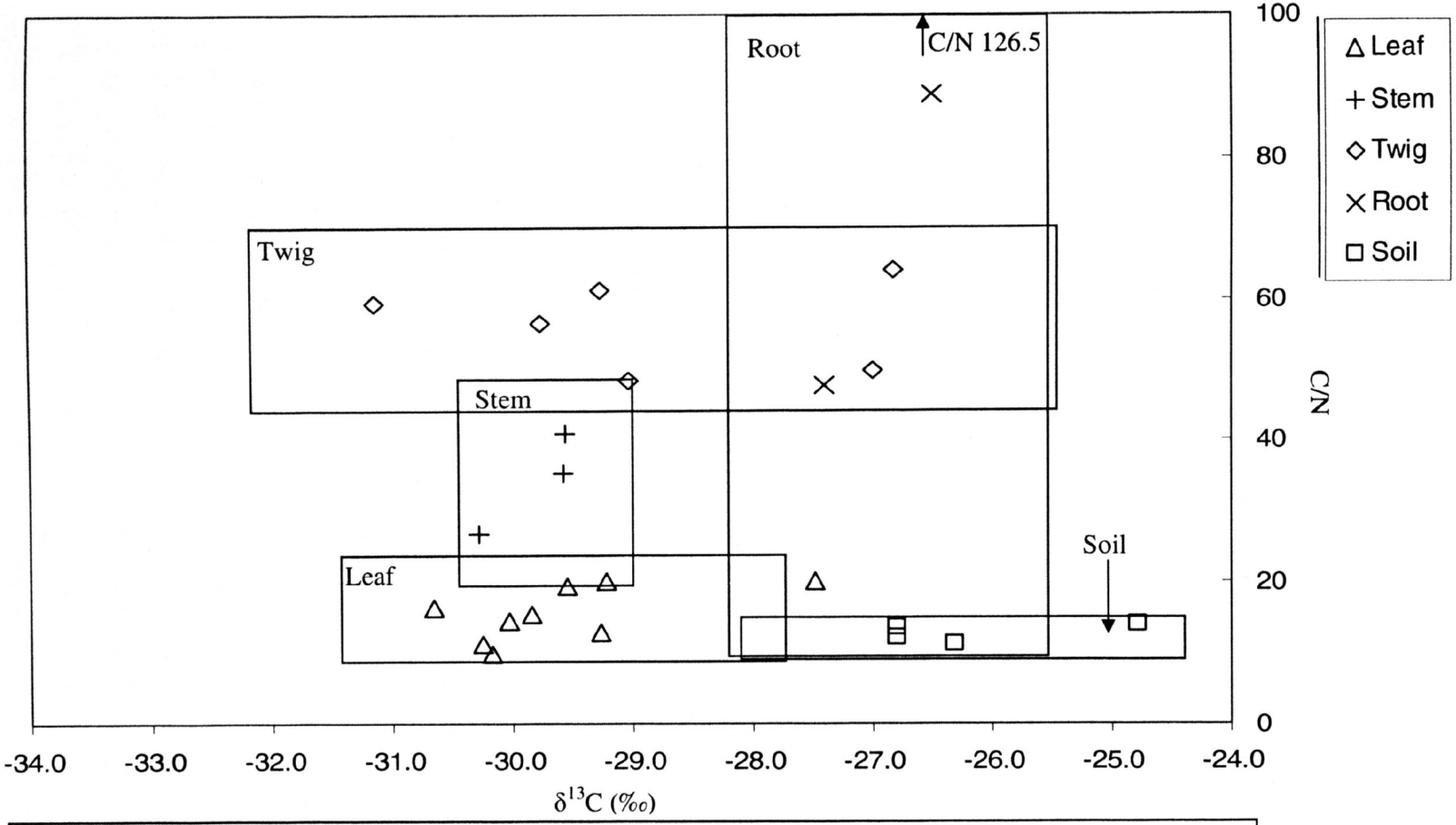


Figure 5.4: *Old House Farm $\delta^{13}C$ and C/N for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species. Boxes indicate the mean ± 2 x standard deviations for each of the material types, showing variability within the data.*

Most photosynthesis, and thus plant growth occurs in the late spring to early autumn months in the UK. Therefore precipitation has been calculated for the Romney Marsh sites from April to September. The Romney Marsh sites have received an average of 316 mm during this period. April to September temperatures for 1970-2000 have also been calculated using the data from the Meteorological Office for the Romney Marsh sites; with a mean of 12.9 ± 5.0 °C for the whole period. The underlying geology, part of the Hastings Bed, is the same for both sites. Since the precipitation, temperatures and underlying geology are similar for both Carter's Farm and Old House Farm it can be assumed that differences between the two sites will be related to local processes and the vegetation community composition.

$\delta^{13}C$ and C/N has been calculated for vegetation and soil samples collected at Carter's Farm and Old House Farm (Figures 5.1, 5.2, 5.3 and 5.4). Exact locations and $\delta^{13}C$ and C/N, can be found in Appendix D; Tables D3 and D4. Site composition where sampling took place can be found in Appendix A; Tables A3 and A4. For Figures 5.1 and 5.3 each sample point represents a unique species of one plant material type. Six key species (*Alnus glutinosa*, *Salix* spp., *Betula* spp., *Dryopteris dilatata*, *Rubus fruticosus*, and *Urtica dioica*) have been labelled. They have been selected since they are abundant and found in many alder carr woodlands (as identified in Rodwell, 1991a). Figures 5.2 and 5.4 show the mean ± 2 x standard deviation of each of the plant material types and soil sample, represented by boxes. This reveals the spread of data within each of the plant material types, and helps to determine whether material types have distinguishable $\delta^{13}C$ and C/N.

At Carter's Farm there is evidence that individual plant species may have specific $\delta^{13}C$ (Figure 5.1). The leaf material shows that *Rubus fruticosus* has the most negative and *Dryopteris dilatata* the least negative $\delta^{13}C$. *Alnus glutinosa*, *Salix* spp. and *Urtica dioica* generally have $\delta^{13}C$ between these two extremes. Examining the woody material reveals once again that *Rubus fruticosus* have the most negative $\delta^{13}C$. Generally *Salix* spp. has less negative $\delta^{13}C$ than *Alnus glutinosa* and *Urtica dioica*. In terms of C/N *Urtica dioica* is the only species that is easily distinguishable, since it has lower C/N compared to the other investigated species.

Although there are wide variations in the $\delta^{13}C$ of individual plant species of the same plant material type (seen in Figure 5.2), there is some evidence for a positive shift in $\delta^{13}C$ from leaf to woody material for the vegetation community as a whole (Figure 5.2). At Carter's Farm, despite considerable variations within the isotope values of individual samples the resultant soil $\delta^{13}C$ remain remarkably consistent, between –27.3‰ and –28.3‰. The soil $\delta^{13}C$ are very similar to the twig and root material $\delta^{13}C$, and towards the least negative leaf $\delta^{13}C$, and seem least influenced by stem material. In terms of C/N there is a clear differentiation between leaf and woody plant material, with leaf having C/N of around 20, and woody material generally having C/N between 30 and 90. Stem material has C/N overlapping the leaf and woody material (from 20 to 80), and this is likely to reflect the 'woodiness' of the stem investigated. The soil C/N is low, typically below 20. This would suggest that the soil material is composed predominantly of leaf material, but may be partly a result of the sampling strategy. As noted in Section 4.3 soil samples were collected in small plastic vials, and therefore may not have contained as much large twig and root material as is present in the community.

Figure 5.3 supports the notion that at Old House Farm $\delta^{13}C$ of plant material may vary for different species. The leaf material reveals that *Salix* spp. generally has less negative $\delta^{13}C$ than the other leaf material, from –27.5‰ to –29.5‰. *Urtica dioica* has similar $\delta^{13}C$ in both the Old House Farm and Carter's Farm records, of around –30.0‰. The twig and root material shows that generally *Salix* spp. has less negative $\delta^{13}C$ than *Alnus glutinosa*. *Urtica dioica* stem material has very similar $\delta^{13}C$ values to those found at Carter's Farm, between –29.5‰ and –30.5‰. In relation to the C/N, *Urtica dioica* once again has the lowest at Old House Farm. The *Salix* spp. leaf C/N appears to be slightly higher, by around 4-5, than other sampled leaf material.

The sampled material from Old House Farm has some general similarities to Carter's Farm in terms of C/N. Figure 5.4 shows that there is a differentiation between the woody and leaf material based on C/N, and stem material lies between the two. The soil C/N is again below 20, indicating they are dominated by leaf material. The $\delta^{13}C$ from Old House Farm do not appear to show the same apparent increase in $\delta^{13}C$ from leaf to woody material found at Carter's Farm. The soil $\delta^{13}C$ appear to be relatively

less negative compared to the majority of the sampled vegetation and also less negative than the soil investigated at Carter's Farm. In this case it appears that the soil $\delta^{13}C$ are particularly influenced by *Salix* spp. plant material, rather than any of the other species. This is likely to be because Old House Farm is dominated by *Salix fragilis* and *S. cinerea* in the upper and lower canopy (see Section 3.4.2). This will be of particular interest when comparing to the *Salix* dominated section of the Hope Farm core in the following chapter.

The assumption that *Salix* spp. is significantly influencing the soil $\delta^{13}C$ needs to be more rigourously tested. For this reason, a crude mixing model has been established using the data collected from Appendices A and D. In this mixing model a number of assumptions have been made, but are necessary to produce an initial estimate of the effects of individual species on the $\delta^{13}C$ of the soil. Firstly, it is assumed that the upper and lower canopies produce the majority of the biomass which is preserved in the soil, so field and ground layer species are not included. It is also hypothesised that leaf material has accounted for 75% of the sampled contemporary sediment, and the remaining 25% is twig material. The estimation of the relative contribution of *Alnus*, *Salix*, and *Betula* are the only tree species investigated, since these are the only ones for which $\delta^{13}C$ and C/N was tested (therefore other tree species which are present have been acknowledged, but are not included in the mixing model). Furthermore it does not take into account other organic carbon sources such as *in situ* bacteria or fungi. It has also been estimated that the upper canopy produces twice as much biomass as the lower canopy. Clearly the methodology described has some severe limitations in terms of accuracy; however it serves as a useful starting point from which to assess the contribution of plant species. Therefore for each contemporary sediment sample a predicted mean, maximum and minimum value has been calculated, using the equation shown in Appendix H.

Figure 5.5 compares the predicted $\delta^{13}C$ of the contemporary sediments to that of the actual $\delta^{13}C$ from Carter's Farm and Old House Farm. The first observation is that all of the predicted $\delta^{13}C$ are 'above' (i.e., more negative than the actual $\delta^{13}C$). This may be due to preservation of material, however it would normally be expected that the $\delta^{13}C$ would decrease. It would therefore be assumed that the other material being

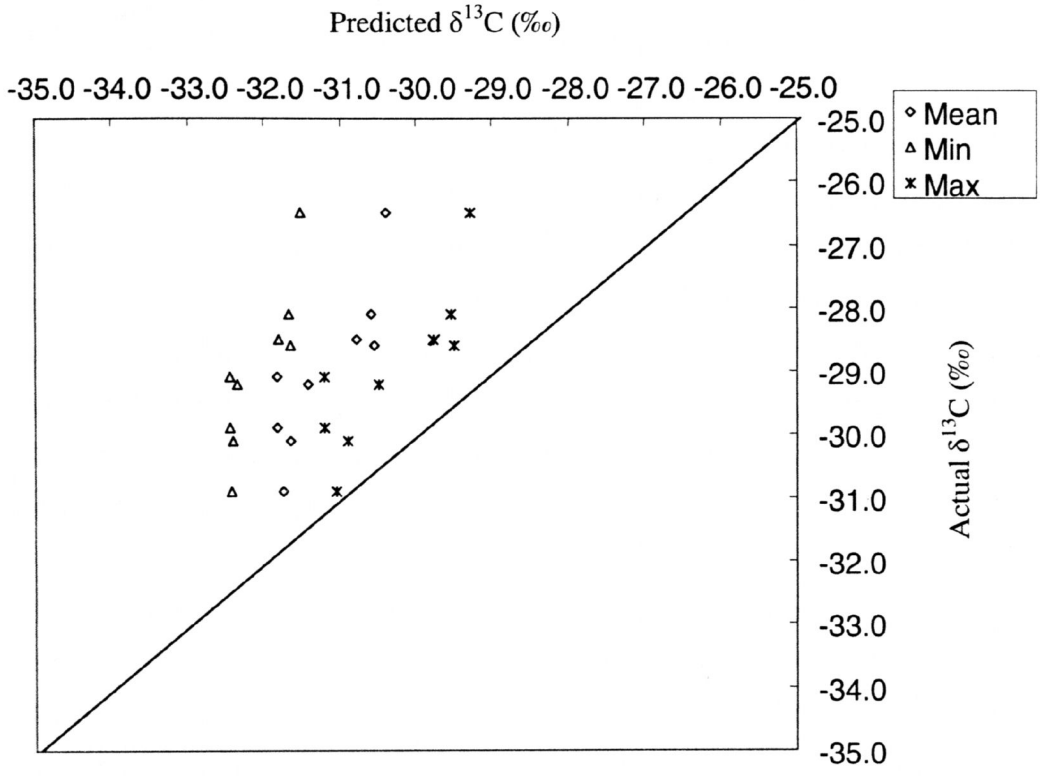


Figure 5.5: *Comparison of predicted mean, minimum and maximum $\delta^{13}C$ to the actual $\delta^{13}C$ of contemporary soils from Carter's Farm and Old House Farm. The diagonal line represents an ideal 1:1 gradient.*

preserved (other than the investigated *Alnus*, *Betula* and *Salix*) is significantly affecting the actual sediment $\delta^{13}C$. Within the predicted results it can be seen that the three main tree species investigated do, up to an extent, seem to influence the contemporary sediment $\delta^{13}C$. However, these results need to be treated with caution due to the limitations in the methodology of the mixing model.

5.2.2 Alder-dominated carr in the Norfolk Broads

The Norfolk Broads alder carr woodlands have been studied to compare to the data from Romney Marsh. The two sites are Calthorpe (Figure 3.7) and Wheatfen (Figure 3.8). Annual precipitation (1971-2000) data from the Meterological Office show that these Norfolk sites receive around 576 mm. The April to September precipitations are 276 mm. The temperatures for this period, averaged from 1971-2000 are 12.8 ± 5.2 °C. The underlying geology for the two sites is chalk. Since the 'summer'

precipitation and temperatures are very similar between the investigated Romney Marsh and Norfolk Broad sites, it can be assumed that systematic changes in the $\delta^{13}C$ and C/N may be a result of changes in underlying geology; vegetation composition and local processes. The chalk is likely to be having the effect of lowering the acidity of the soil, and its porous nature may be limiting the groundwater availability. If this is the case, and there is a stress operating on the vegetation community, then the $\delta^{13}C$ are likely to become less negative. At Wheatfen there is the possibility that the alder carr environment is influenced by tides, due to its proximity to the Yare (Waller *et al.*, 1999). This would also have the effect of increasing the $\delta^{13}C$. The potential stress factors can be easily tested by comparing the data from Norfolk sites with each other and with the Romney Marsh sites.

Figure 5.5 shows the $\delta^{13}C$ and C/N of leaf, stem, twig and root material and soil sampled at Calthorpe. *Alnus glutinosa*, *Salix* spp., *Betula* spp., *Dryopteris dilatata*, *Rubus fruticosus*, and *Urtica dioica* are shown on the graph to show whether individual species are particularly influential on the final soil isotope and C/N. The Calthope data appears to contradict the findings of Romney Marsh. The least negative leaf $\delta^{13}C$ are *Rubus fruticosus* and *Urtica dioica*, which have previously been shown to have more negative $\delta^{13}C$. This is far from conclusive however, since there is only one sample of each plant type. The wood material shows once again that *Salix* spp. has less negative $\delta^{13}C$ than *Alnus glutinosa*, however the sampled *Rubus fruticosus* has much less negative $\delta^{13}C$ than might be expected based on the Romney Marsh samples. From C/N alone it is not possible to differentiate between plant species based on the Calthorpe record. However, the *Salix* spp. wood C/N is around 20 higher than other sampled woody material.

The results from Calthorpe suggest that there is a clear distinction between the C/N of leaf and non-leaf material (Figure 5.6). C/N of leaf material is consistently between 10 and 25, whereas the non-leaf material is much more variable, between 50 and 80. The soil material once again has low C/N, similar to the leaf material. The increase in $\delta^{13}C$ from leaf to stem to wood components is not distinguishable at this site. Similarly to the Romney Marsh sites, there is great variability in the $\delta^{13}C$ of

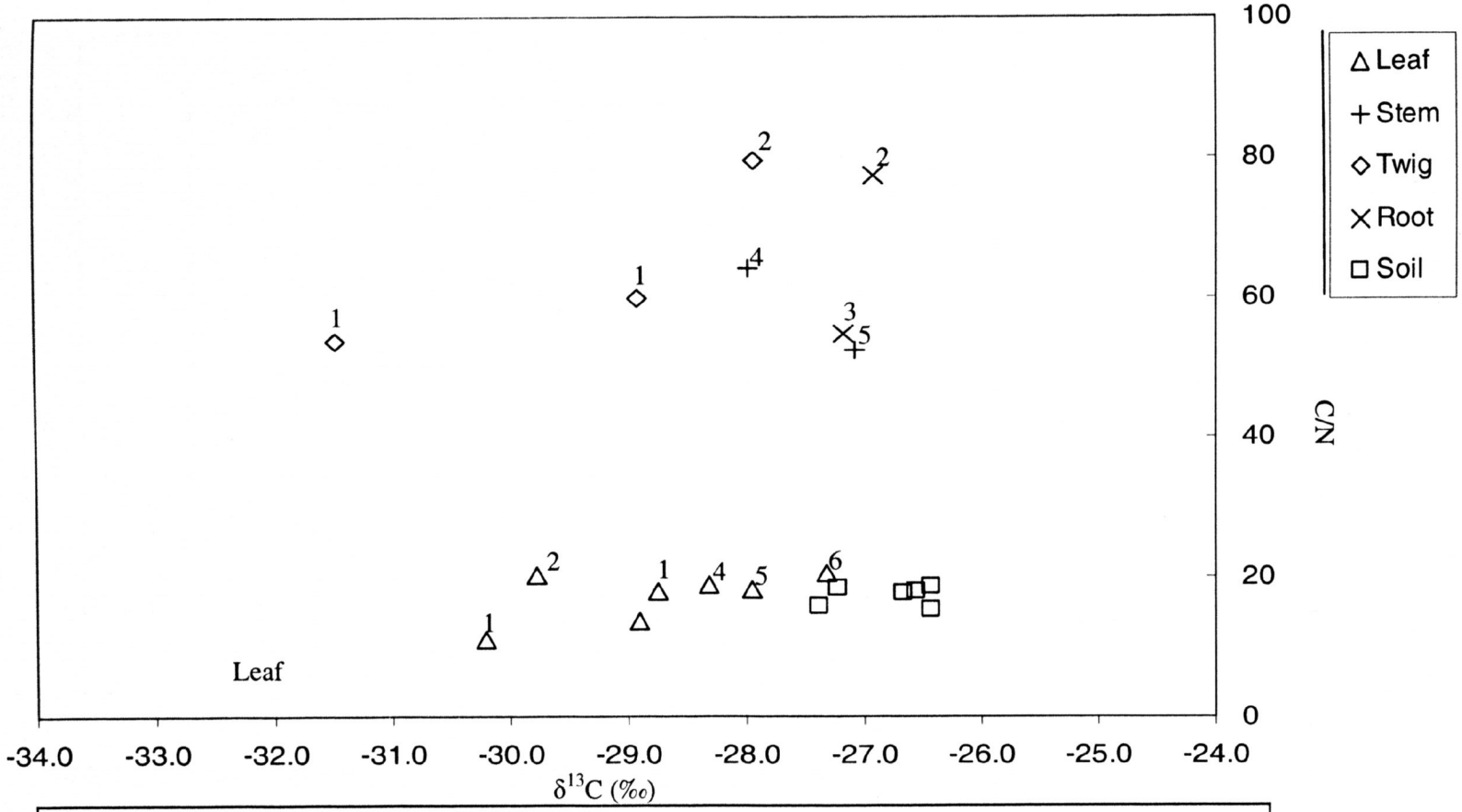


Figure 5.6: *Calthorpe $\delta^{13}C$ and C/N for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species. (1)* Alnus glutinosa *(2)* Salix spp. *(3)* Betula spp. *(4)* Dryopteris dilatata *(5)* Rubus fruticosa *(6)* Urtica dioica.

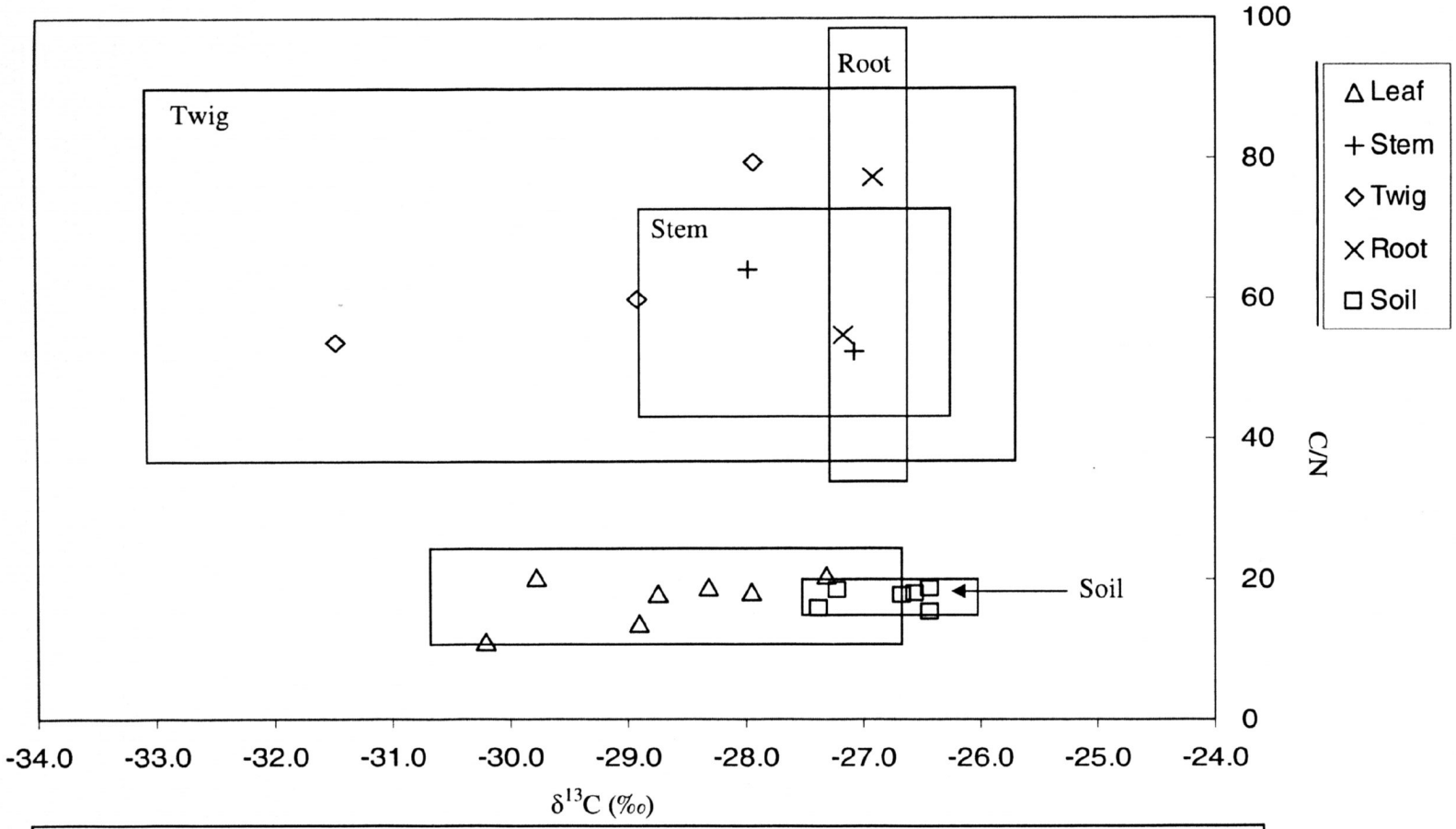


Figure 5.7: *Calthorpe $\delta^{13}C$ and C/N for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species. Boxes indicate the mean ± 2 x standard deviations for each of the material types, showing variability within the data.*

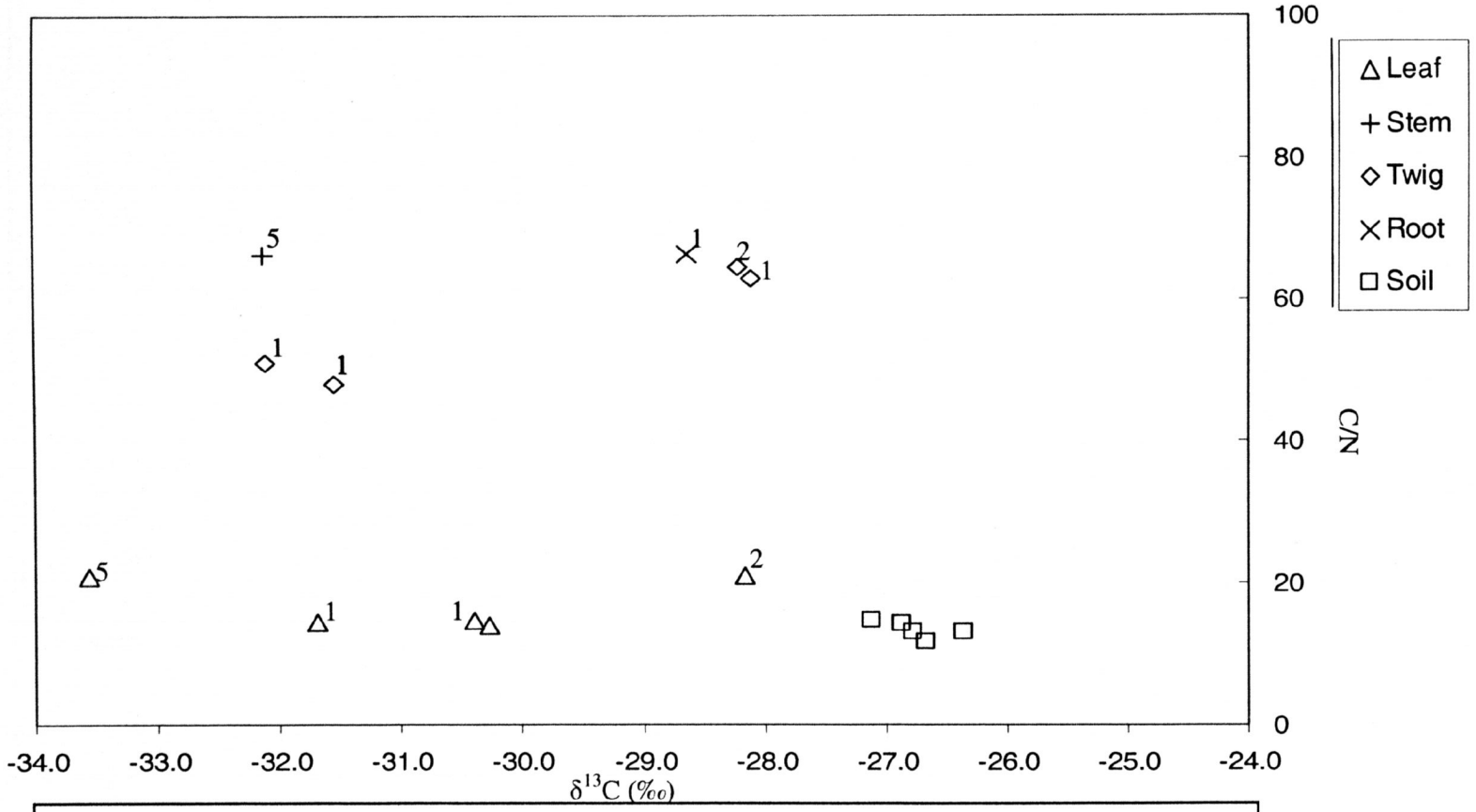


Figure 5.8: *Wheatfen $\delta^{13}C$ and C/N ratio for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species.. (1)* Alnus glutinosa *(2)* Salix spp. *(3)* Betula spp. *(4)* Dryopteris dilatata *(5)* Rubus fruticosa *(6)* Urtica dioica.

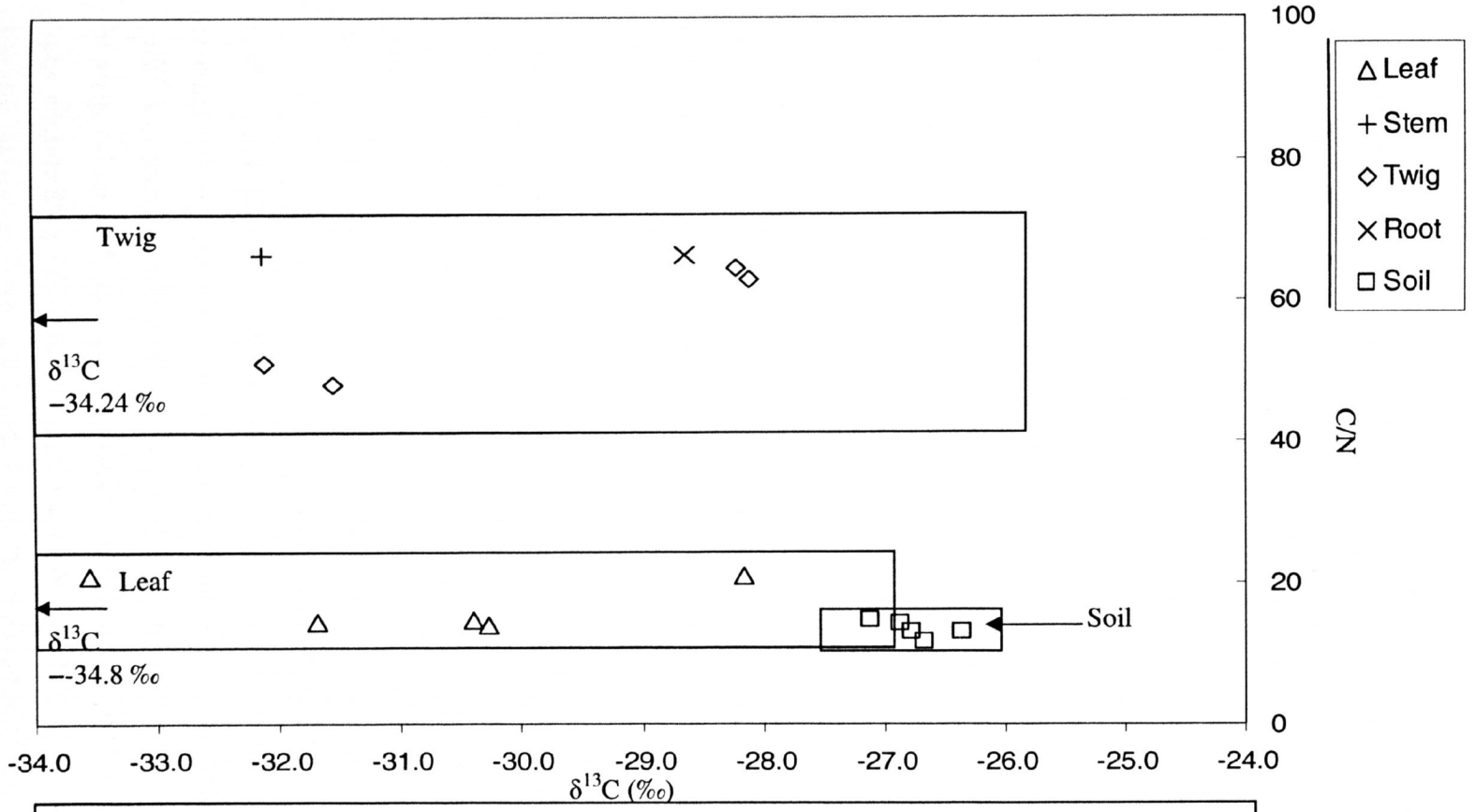


Figure 5.9: *Wheatfen $\delta^{13}C$ and C/N for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species. Boxes indicate the mean ± 2 x standard deviations for each of the material types, showing variability within the data.*

different types of plant material. The soil $\delta^{13}C$ however are consistently between –26‰ and –27.5‰.

Wheatfen (Figure 5.7) reveals that *Rubus fruticosus* has more negative $\delta^{13}C$ than *Alnus glutinosa*; while *Salix* spp. have the least negative, for both the leaf and woody material. There is little differentiation between species in terms of the C/N at this site. The distinction between leaf and twig material using C/N is apparent (Figure 5.8). The apparent increase in $\delta^{13}C$ found at Carter's Farm from leaf to wood material is not obvious at Wheatfen, although this may be in part to the smaller sample size. One of the striking outcomes from the Wheatfen $\delta^{13}C$ is the degree of variability of the leaf material. Although similar species have been sampled for each vegetation community there is a spread of –28.2‰ to –33.6‰ compared to –27.3‰ to –30.2‰ for Calthorpe. This is unlikely to be a local process or climatic control, as there has been no knock-on effect to the other biomass components or the resultant soil $\delta^{13}C$. Furthermore, stresses such as increases in salinity and less availability of water would have led to less negative $\delta^{13}C$ rather than the observed negative shift. This highlights the need for many samples to be collected in this type of investigation since microscale processes and natural variability may lead to great changes in the $\delta^{13}C$ of the sampled material.

When examining all the alder carr data together (Figure 5.9) it is possible to see that leaf and woody material can be generally differentiated based on their C/N. Root, twig and stem material cannot be differentiated based on C/N or $\delta^{13}C$, however root material tends to have less negative $\delta^{13}C$. There is no obvious evidence for an increase in $\delta^{13}C$ from leaf to woody material. Soil $\delta^{13}C$ are relatively positive from –25.3‰ to –28.5‰ from the contemporary alder carr environment, when compared to the overall plant material from which it is generated. When 'correcting' the plant material and soil samples, it has been assumed that all have fixed their carbon, in a permanent state, at the time of sampling. It is likely in reality that leaf material will be younger than stem, root and twig material. However, the age difference is unlikely to be considerable, since thinner twigs and roots have been preferentially selected. Equally the soil samples must be older than the sampled leaf, twig, root and stem material.

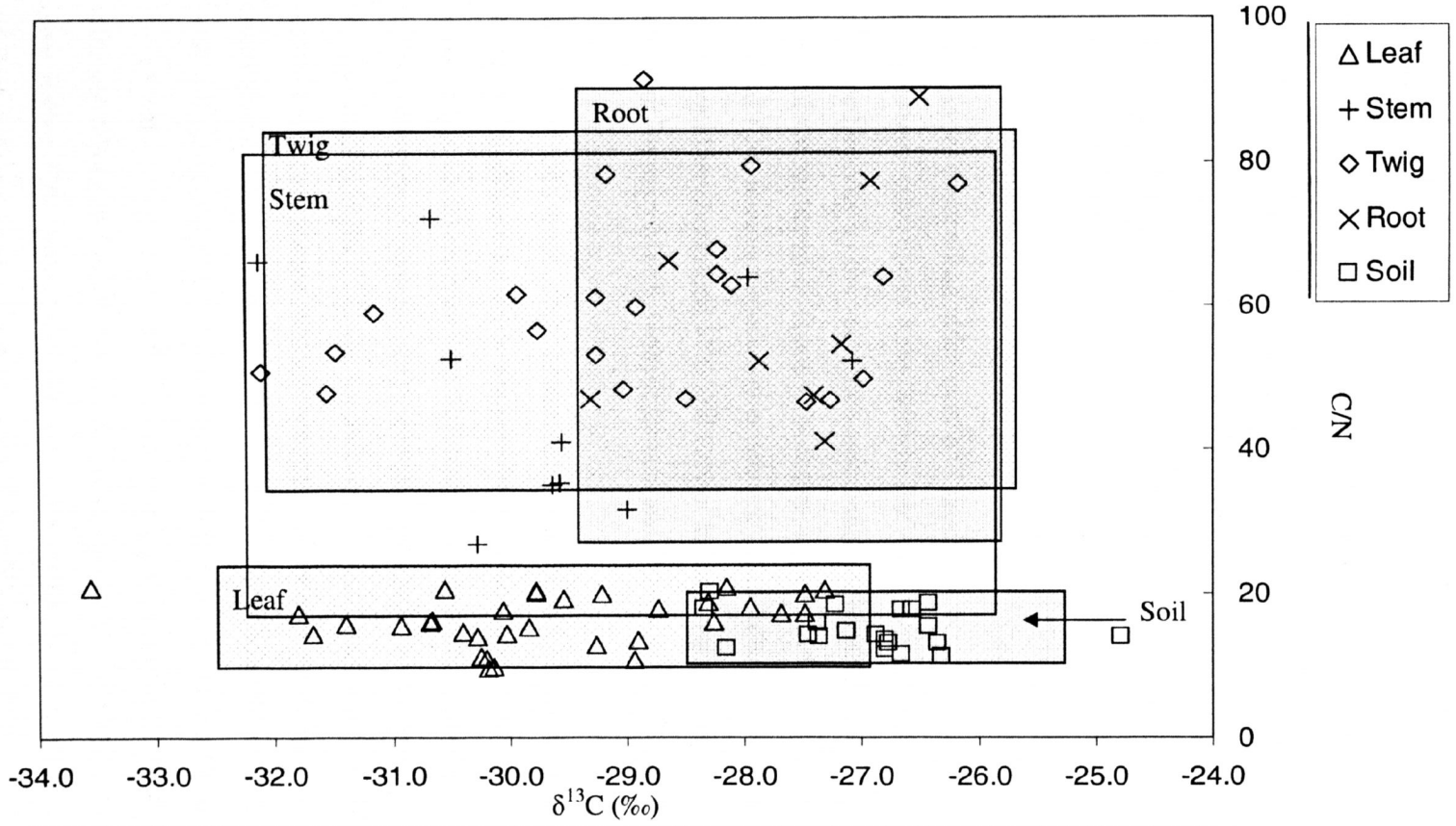


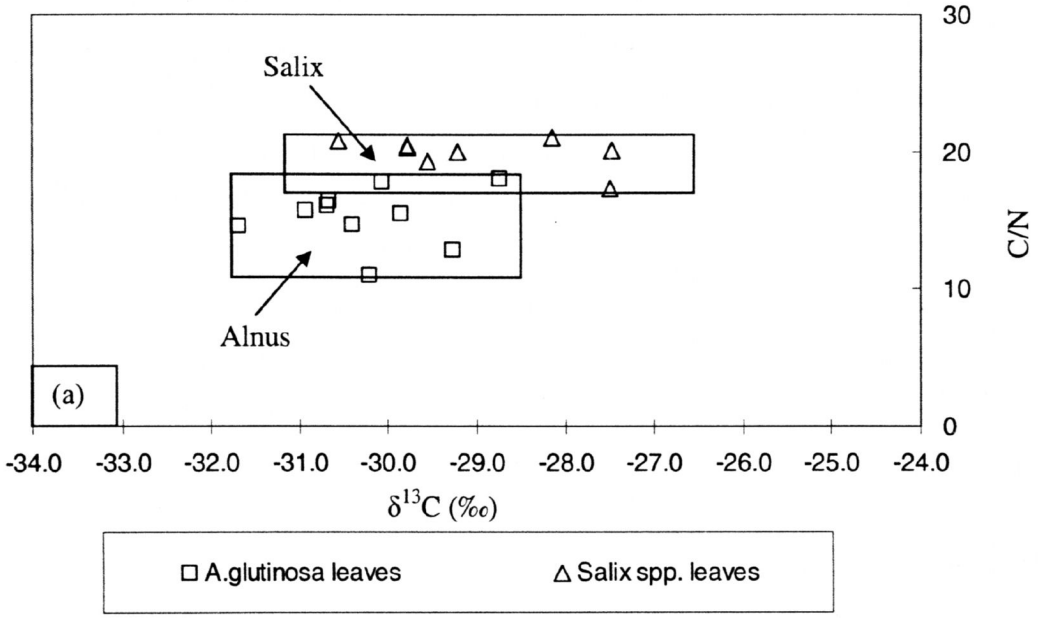
Figure 5.10: All alder carr (Romney Marsh and Norfolk) *$\delta^{13}C$ and C/N for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species. Boxes indicate the mean ± 2 x standard deviations for each of the material types, showing variability*

The rate of deposition in this case will have an impact on the age of the investigated soil. Using the $\delta^{13}C$ corrector of McCarroll and Loader (2004) it can be seen that since about 1960 for each decade the soil has been deposited the soil will appear to have a less negative $\delta^{13}C$ of 0.3‰. If, for example, the average age of the sampled soil is 30 years old the $\delta^{13}C$ of the atmospheric air (from which the plants fixed their carbon) will be more negative by 0.9‰. In this situation it would appear that soil in alder carr communities are dominated by leaf material, and specifically greatly influenced by *Alnus glutinosa* and *Salix* spp. Although this has not been done in this study, the soil could be dated which would enable this potential problem to be overcome.

5.2.3 Factors controlling alder carr $\delta^{13}C$ and C/N

The previous subsections have shown that the resultant soil $\delta^{13}C$ and C/N are influenced heavily by the vegetation community in which they are created. Despite a degree of variability of $\delta^{13}C$ and C/N within the living biomass of the woodland soil $\delta^{13}C$ and C/N remain remarkably consistent. This subsection examines the factors which could be controlling $\delta^{13}C$ and C/N of alder carr plant and soil material, using data from Romney Marsh, Norfolk Broads and elsewhere in the UK.

One of the outcomes from investigating the Romney Marsh sites has been the potential for determing *Salix* domination in alder carr communities. To test this further Figure 5.10 examines the differences between *Alnus glutinosa* and *Salix* spp. for the investigated contemporary fieldsites. Although there is some overlap between the two species, *Salix* $\delta^{13}C$ are, on average, 1.2‰ less negative for the sampled leaf material and, on average, 1.8‰ less negative for the sampled twig and root material compared to *Alnus glutinosa*. This implies that in a *Salix* dominated alder carr the final soil isotope would in turn be higher. However, the variability associated from leaf to leaf or twig to twig of the same species is significant, which would hamper efforts to reconstruct exact past vegetation composition. *Salix* also have a tendency to have higher C/N than *Alnus* (Figure 5.10), which is as a result of having less nitrogen, rather than more carbon stored in the plant material.



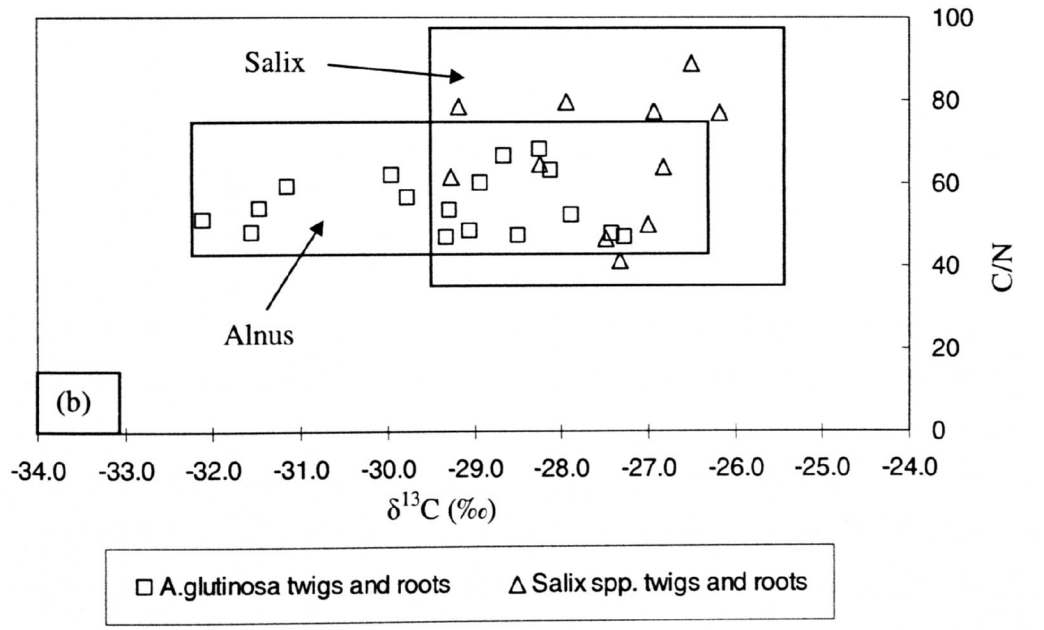


Figure 5.11: *Comparison of $\delta^{13}C$ and C/N ratios for* Alnus glutinosa *and* Salix *spp. (a) compares the leaf material and (b) compares the woody material (twig and root). Boxes indicate the mean ± 2 x standard deviations for each of the material types, showing variability within the data.*

There have been very few studies of the $\delta^{13}C$ and C/N of contemporary alder carr environments. Mackie (2004) sampled leaf material from a variety of plant species around Arisaig, north-west Scotland. The bedrock around Arisaig is metamorphic (Mackie *et al.*, 2005), mainly gneisses and granulites, and receives annual precipitation of 2277 mm. The April to September average is 745 mm, while the temperature for this period is 11.1 ± 3.6 °C.

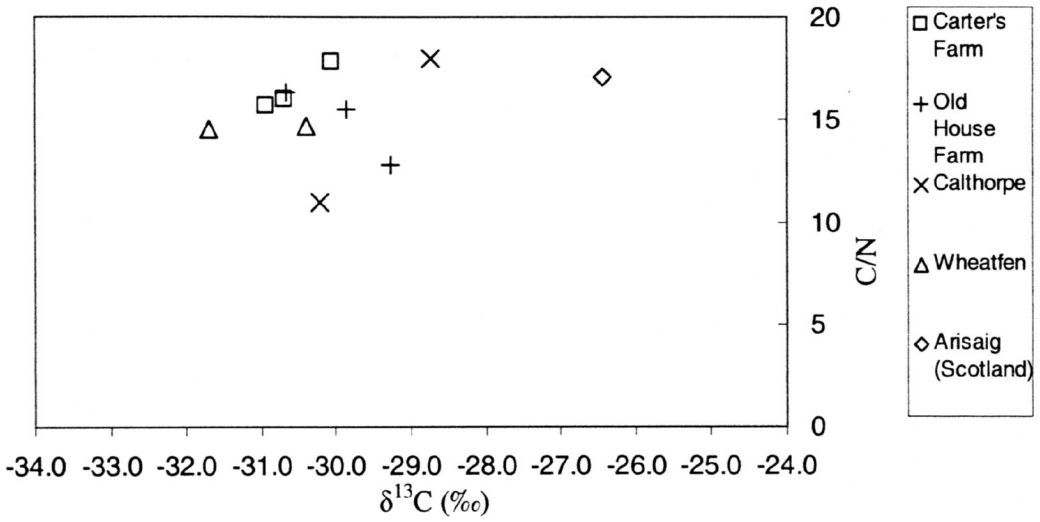


Figure 5.12: *Comparison of the* Alnus glutinosa leaves $\delta^{13}C$ *and C/N from Romney Marsh, Norfolk and Arisaig.*

Differences in the precipitation and temperature between the Norfolk and Romney Marsh sites have been shown to be small, especially when considering the April to September averages (the time when most photosynthesis is occurring). Examining Figure 5.11 has shown that the *Alnus glutinosa* leaf $\delta^{13}C$ are between –28.7‰ and –31.7‰ for the south-east England sites. The $\delta^{13}C$ of the Scottish *Alnus glutinosa* leaves are noticeably less negative than those in Romney Marsh and Norfolk (a shift of around 3‰). High temperatures and low precipitation levels would cause the closure of stomata (e.g., Llorens *et al.*, 2004), which lead would lead to less negative $\delta^{13}C$. This is not the case in Scotland since the temperature is in fact lower, and the precipitation levels are higher. For this reason it is unlikely that the climate is the dominant influence upon the $\delta^{13}C$ of the *Alnus glutinosa* leaves. The bedrock, which is impermeable, may be leading to increased run off and lower ground water storage

levels. Alder woodlands need to be in waterlogged conditions (McVean, 1953) and so if groundwater levels are lower then there will be an environmental stress on the vegetation. This environmental stress could then be causing the apparent positive shift in $\delta^{13}C$.

In summary it has been shown that there are three key controls on the $\delta^{13}C$ signatures of alder carr environments. Firstly, different plant material types have different isotope signatures. Wood material has much higher C/N than leaf material, and, in general, than stem material. The variability in the C/N of stem material may be in part due to the 'woodiness' of its composition. There is some evidence to suggest that woody material also have slightly less negative $\delta^{13}C$ than leaf material, however this is preliminary evidence, and requires further investigation. Secondly, the species composition of the vegetation community has a probable effect on the $\delta^{13}C$ signatures of their soils. In this investigation *Salix* spp. has been identified as a key species, with on average less negative $\delta^{13}C$ than much of the vegetation sampled. This is most clearly seen in the Carter's Farm, Old House Farm and Wheatfen investigations. It should be noted however that there is a great deal of natural variability between samples and therefore a less negative $\delta^{13}C$ value will not necessarily represent a *Salix*-dominated community. The third key potential control on the $\delta^{13}C$ signatures of alder carr environments is environmental stresses. Changes in precipitation and temperature have not been shown to significantly affect the isotope of alder carr communities, however this must remain a consideration for the palaeoenvironmental record.

5.3 Saltmarsh

The sampling strategy in Romney Marsh saltmarsh has been designed to compare the relationship between the $\delta^{13}C$ and C/N of the contemporary plant material and their soils. Research has been put in context of other saltmarsh sites including saltmarsh found in the Humber, Mersey and Severn estuaries in the UK.

5.3.1 Saltmarsh in Romney Marsh

Figures 5.12 and 5.13 show the $\delta^{13}C$ and C/N of the sampled leaf, stem, grass and *Salicornia* material, as well as the contemporary soil samples. Leaf material has

much more variable C/N than in the alder carr environment, with values as high as 46, although most leaf samples do have C/N around 20. The stem material is typically variable, often due to the 'woodiness' of the sample involved. *Salicornia* stems have C/N which is similar to leaf material, while the grasses have C/N between 15 and 45. There appears to be little distinction between the $\delta^{13}C$ of the different plant material types. From this study plant material from saltmarsh environments have $\delta^{13}C$ typically in the range of –22.5‰ to –26.5‰, which is noticeably higher than for the alder carr plant material. The reason for this shift could be linked to the salinity of the site, and thus to stress on the plants leading to reduced uptake of ^{13}C, thus increasing the $\delta^{13}C$ (Brugnoli and Bjorkman, 1992). Other research (e.g., Twiddy, 1996) has found that the relationship between $\delta^{13}C$ of plant material and salinity to be less clear. In the Rye saltmarsh tidal creeks supply sea water to most parts of the saltmarsh, so the gradational pattern from 'low' to 'high' saltmarsh plant species is less easy to distinguish. For this reason the salinity induced stress upon the vegetation is less easy to distinguish. One striking observation in Figure 5.13 is the difference between the soil and plant $\delta^{13}C$ signatures. It is clear that the C_3 plants sampled in this investigation are not the main contributors to the final soil production. In fact, there was very little organic carbon in the silt itself, around 4-9%, compared to typical values of 30-40% in the alder carr woodlands. The shift in $\delta^{13}C$ is far too great to be linked with post-depositional fractionation, and so two main possibilities remain. The first is the abundance of *Spartina townsendii* (a C_4 plant). This is found elsewhere in the marsh and may be being trapped by roots (Howorth, 1993). The second is through tidally driven detritus, such as marine algae which have much less negative $\delta^{13}C$ (around -22‰) (Prahl *et al.*, 1980). This has been shown to occur in other in other estuaries, such as the Pearl River in China (Zong *et al.*, 2006) and is more likely.

Figure 5.12 examines whether individual plant species have specific $\delta^{13}C$ and C/N. It shows that low saltmarsh species, such as *Salicornia* spp. have much the same isotope value as higher saltmarsh species such as *Aster tripolium* and *Seriphidium maritimum*. While there is no evidence to suggest that high and low saltmarsh species would have different isotope, it is plausible that the increased stress from salinity would cause less negative $\delta^{13}C$ (Section 2.5.2).

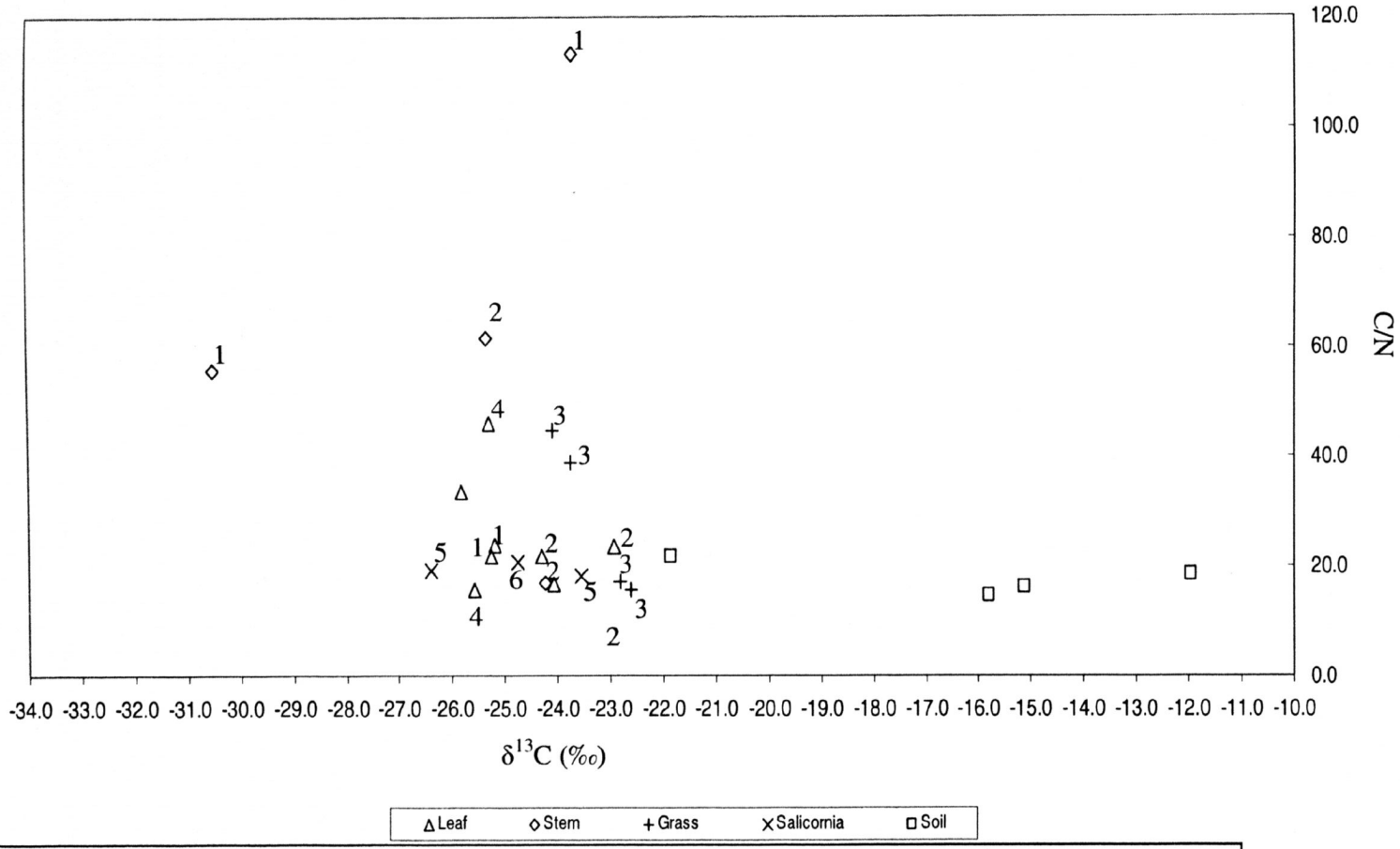


Figure 5.13: *Rye Saltmarsh $\delta^{13}C$ and C/N ratio for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species.. (1)* Aster tripolium *(2)* Seriphidium maritimum *(3)* Festuca rubra *(4)* Limonium vulgare *(5)* Salicornia ramossisima *(6)* Salicornia fragilis.

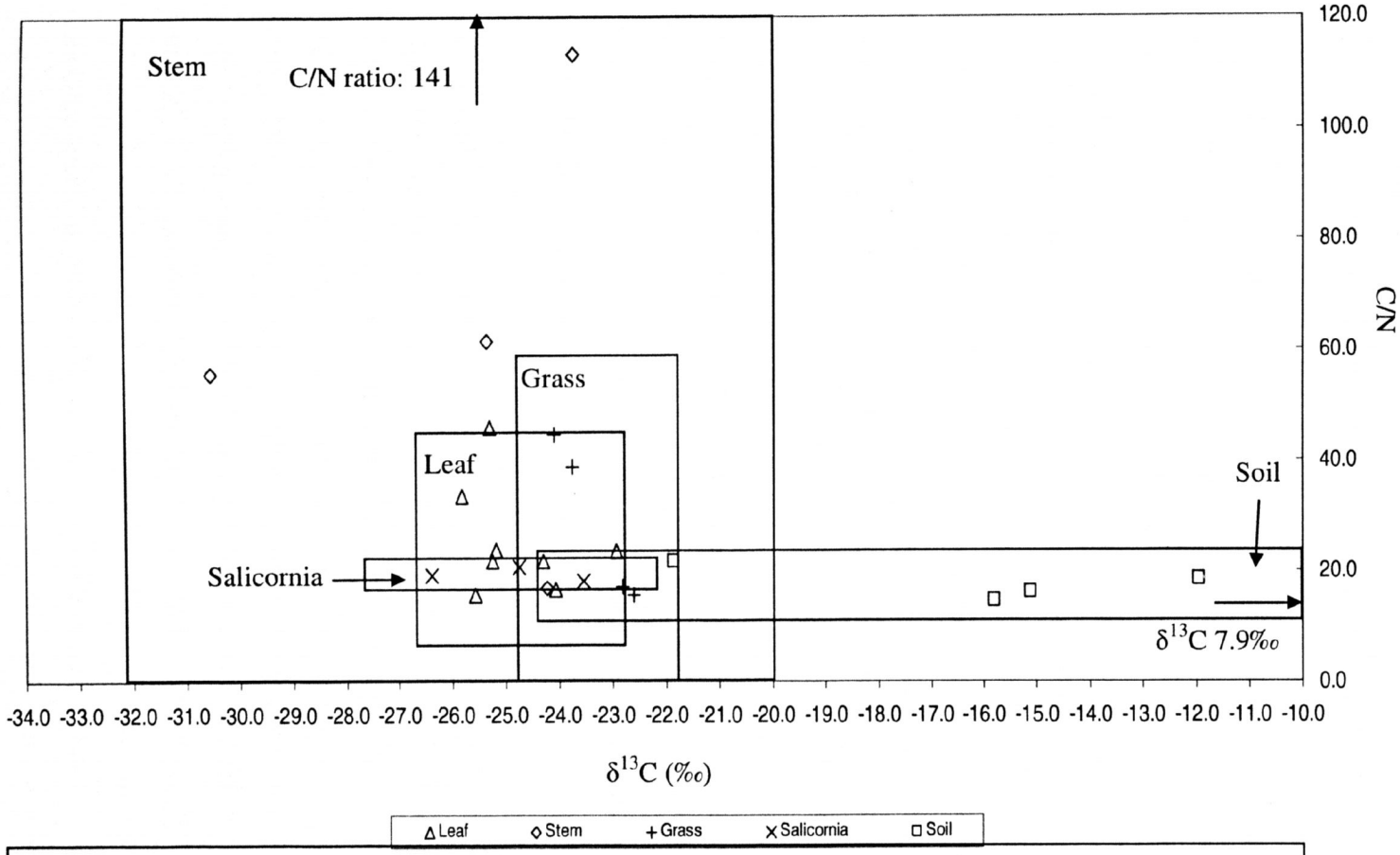


Figure 5.14: *Rye Saltmarsh $\delta^{13}C$ and C/N ratio for leaf, stem, twig, root and soil material. Each sample point represents plant material from an individual species. Boxes indicate the mean ± 2 x standard deviations for each of the material types, showing variability within the data.*

5.3.2 Factors controlling saltmarsh $\delta^{13}C$ and C/N

Studies of contemporary plants and surface samples from the Humber (Andrews, 2000), the Mersey (Wilson, 2004; Wilson *et al.*, 2005a; b) and the Severn (Allen *et al.*, 2007) estuaries are used to supplement the study in Romney Marsh. Bouchard and Lefeuvre, (2000) also examined C/N of some saltmarsh plants from northern France, but did not complete any isotope studies. Of these studies only Wilson *et al.*, (2005a) and Allen *et al.*, (2007) have examined the contemporary $\delta^{13}C$ and C/N of saltmarsh plant material. A high and low marsh plant species, *Eltrigia atherica* and *Aster tripolium*, were examined at both sites. After correction of $\delta^{13}C$ to pre-Industrial levels the leaf $\delta^{13}C$ of *A. tripolium* were identical, and *E. atherica* material was slightly less negative (+ 0.6‰) in the Romney Marsh samples. Low saltmarsh plants are adapted to highly saline conditions, and therefore it is less likely that climatic stresses, such as reduced precipitation, will influence the $\delta^{13}C$ values of the plant. Higher saltmarsh plants, such as *E. atherica*, are theoretically more susceptible to influence, and the limited data from Romney Marsh and the Severn Estuary supports this theory. However, since there is very little difference in $\delta^{13}C$ of high and low saltmarsh plant species, together with the data from *Phragmites australis* in a saline environment (Twiddy, 1996) it is hard to quantify the effect of salinity.

Other studies in the UK have focused on contemporary sediment samples in saltmarsh environments. Figure 5.14 shows that in the Rye saltmarsh the sediment $\delta^{13}C$ are much less negative than in any of the other estuary studies, and in fact are more comparable with marine sediments (e.g., Middelburg and Nieuwenhuize, 1998). This is in part due to the C4 plant *Spartina townsendii*, but is likely also reflect allochthonous marine plankton. Different saltmarsh appear to have slightly differing $\delta^{13}C$ signatures. The Mersey estuary data (Wilson *et al.*, 2005a) shows a change in $\delta^{13}C$ in relation to altitude above the tidal frame, thus linked to the amount of allochthonous material, while the Humber estuary data (Andrews, 2000) in general have higher C/N than the other two UK sites. Overall it is possible to see that saltmarsh sediments have much positive $\delta^{13}C$ than alder carr environments, and this information will be useful in distinguishing environments in both the Hope Farm and Little Cheyne Court cores.

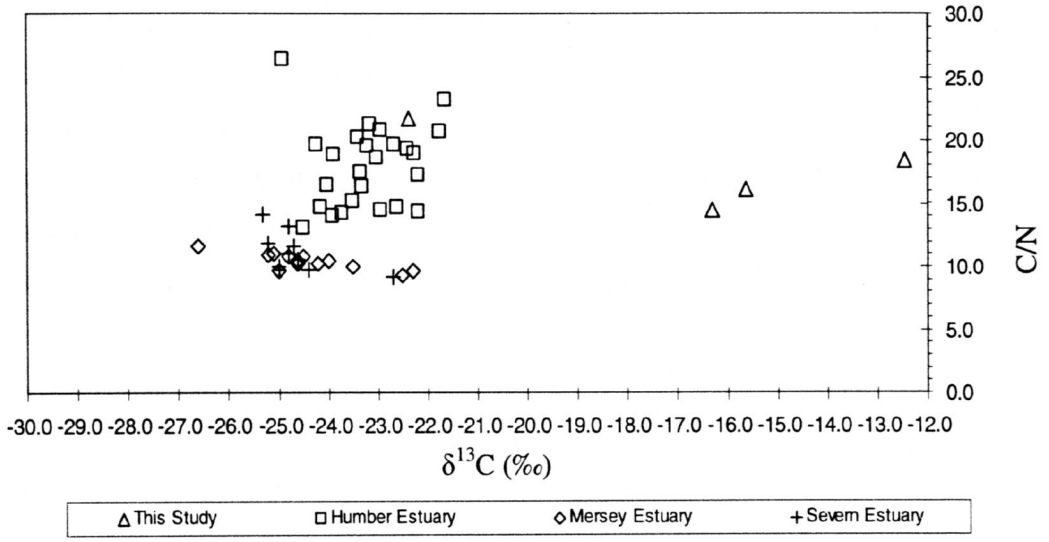


Figure 5.15: *Comparison of the contemporary surface sediment $\delta^{13}C$ and C/N from Romney Marsh, Humber Estuary, Mersey Estuary and Severn Estuary saltmarshes.*

5.4 Conclusions

This chapter has examined the use of $\delta^{13}C$ and C/N in alder carr and saltmarsh environments using data collected as part of this study and from other UK sites. It has been seen that there is a clear distinction between saltmarsh and alder carr environments within the sedimentary record. Within these environments, certain plant species are important in influencing the final soil isotope and C/N. Other environmental stresses, such as water availability and salinity, have been found to have an effect on the $\delta^{13}C$ of the plant material and resultant soils. This must therefore be an important consideration in palaeoenvironmental reconstructions. The following chapter will apply the knowledge gained from the contemporary record to the Hope Farm and Little Cheyne Court main peat records.

Chapter 6: Results from the palaeonvironmental record

6.1 Introduction

This chapter examines bulk organic $\delta^{13}C$ and C/N of the cores from the Romney Marsh depositional complex; Hope Farm and Little Cheyne Court. It compares the $\delta^{13}C$ and C/N of organic material within the cores together with pollen analyses determining whether individual vegetation communities have distinct $\delta^{13}C$ signatures. It also compares the $\delta^{13}C$ and C/N of the Romney Marsh sediments to palaeoenvironmental investigations in the UK. Interpretations will be made in relation to the knowledge gained from the contemporary record described in Chapter 5.

6.2 Little Cheyne Court

The Little Cheyne Court core has previously been the subject of diatom and pollen reconstruction by Waller *et al.* 1999. The main marsh peat records at 4100 years of data regarding peat deposition in the centre of Walland Marsh. Contiguous 1 cm sampling through the core provides 136 samples for $\delta^{13}C$ and C/N analysis, covering five vegetation communities (saltmarsh, herbaceous fen, poor fen, Cyperaceae-dominated and bog and described from pollen (Waller *et al.*, 1999). Figure 6.1 compares the pollen record to the $\delta^{13}C$ and C/N from this research. Figures 6.2 and 6.3 illustrate the $\delta^{13}C$ and C/N of the peat of Little Cheyne Court from 1200-5300 cal. years BP. Zones were the same as those identified in Waller *et al.* 1999, and are based in the palynology of the sampled peat. In this way it is possible to compare distinct vegetation communities with their $\delta^{13}C$ and C/N to determine whether there are changes or variability within each community and whether vegetation communities have distinct isotope geochemistry.

6.2.1 Little Cheyne Court core $\delta^{13}C$ and C/N

Zone 1 (below 386 cm)

The pollen record (see Figure 6.1) suggests Zone 1 vegetation is dominated by saltmarsh conditions, with high values of Chenopodiaceae, Cyperaceae and Poaceae recorded (Waller *et al.*, 1999). For the lowermost part of the peat in the core

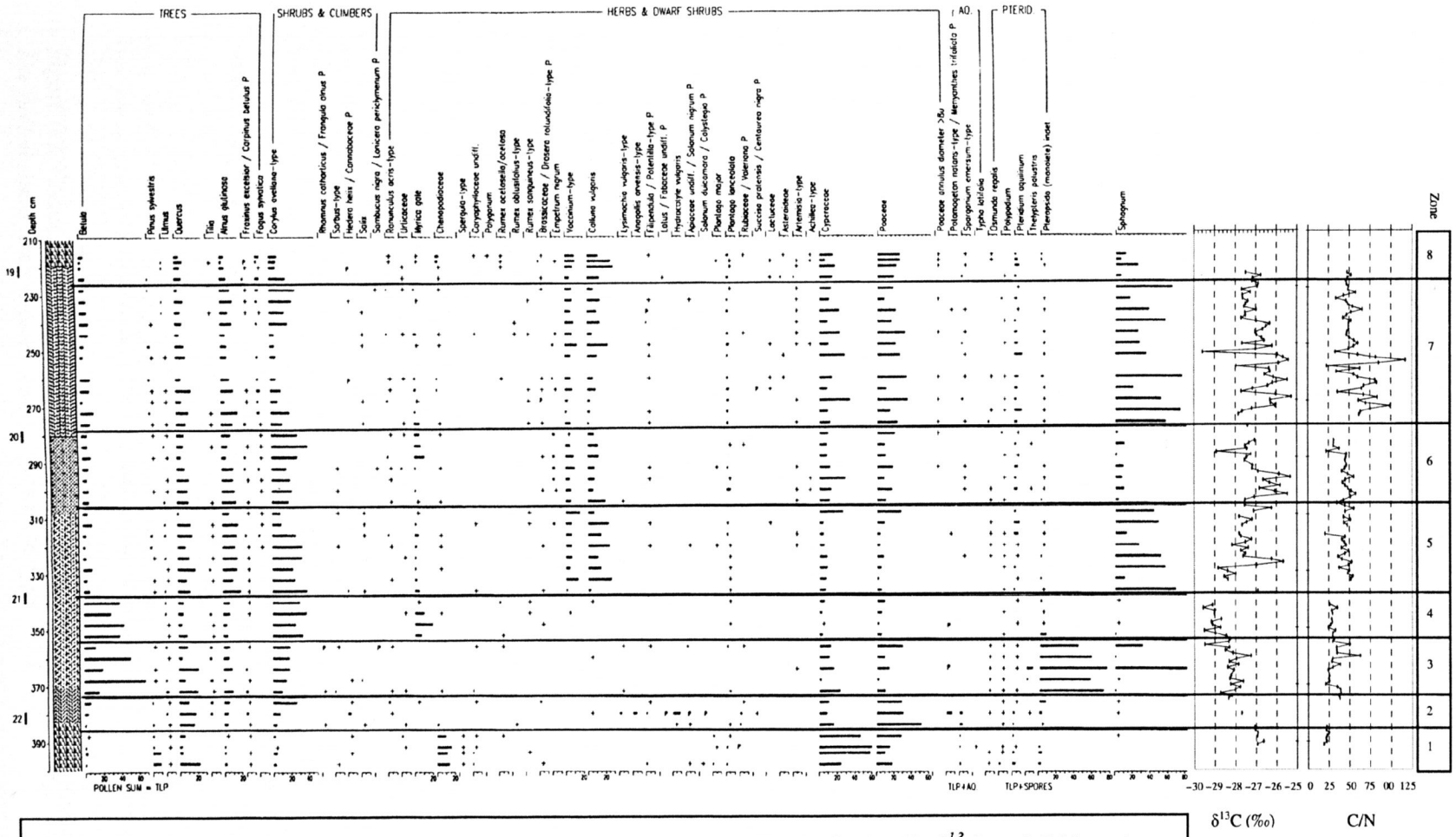


Figure 6.1: *Little Cheyne Court percentage pollen diagram from (Waller* et al., *1999); $\delta^{13}C$ and C/N against depth. The + and P symbols indicate <1% total land pollen (TLP). The 8 pollen zones are indicated.*

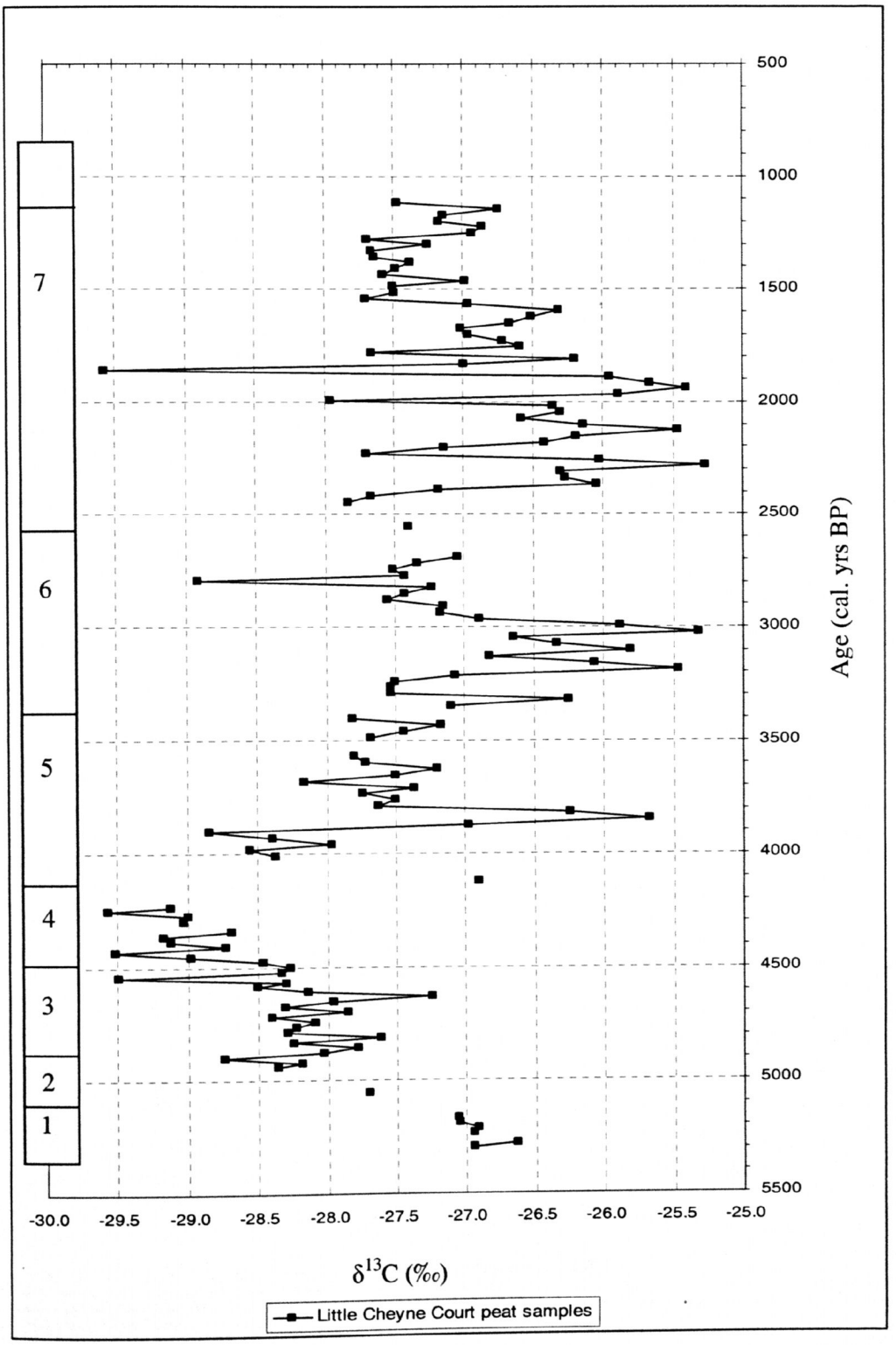


Figure 6.2: *Change in $\delta^{13}C$ through the Little Cheyne Court core through time. The pollen zones are indicated and correspond to Figure 6.1.*

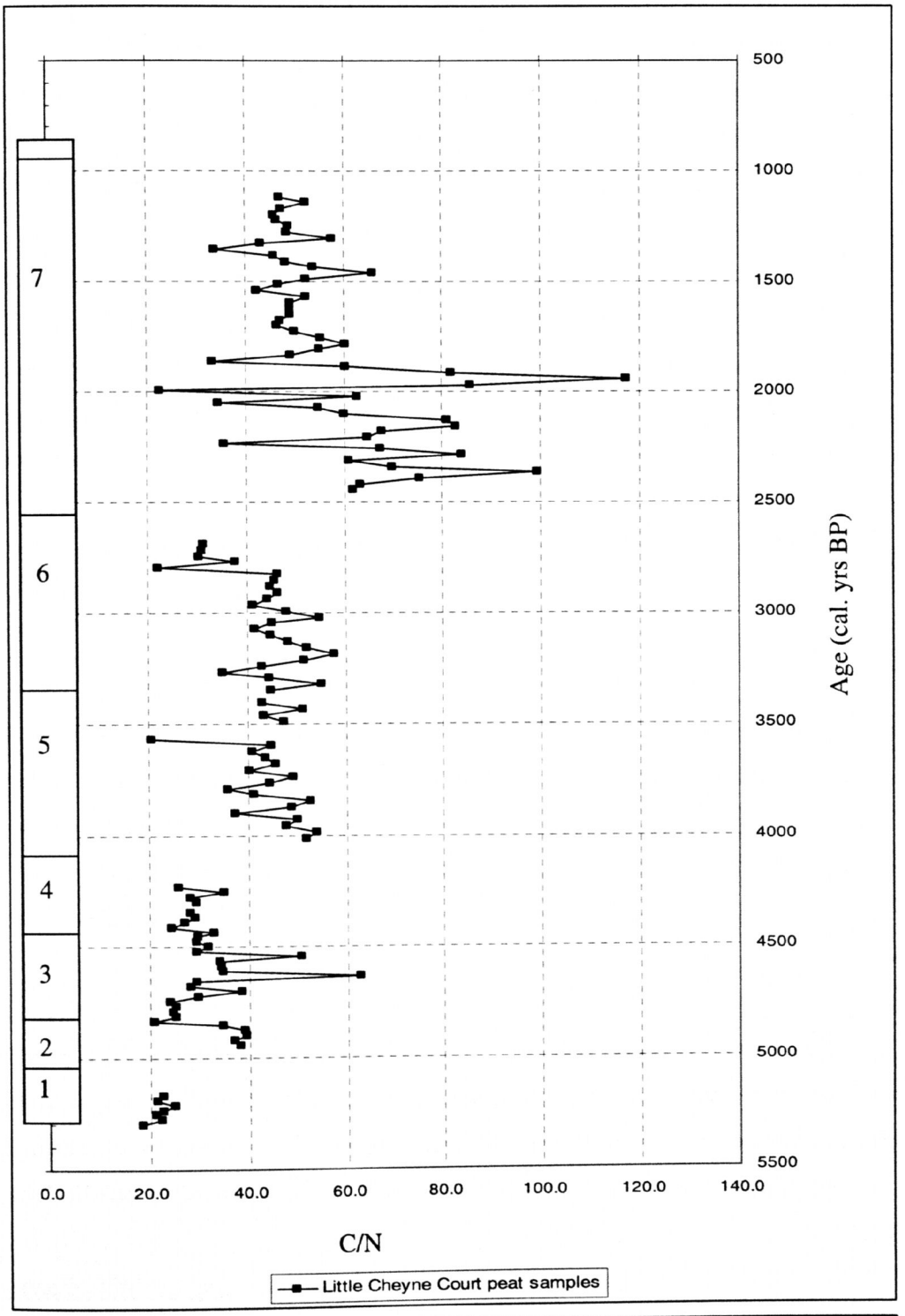


Figure 6.3: *Change in C/N through the Little Cheyne Court core through time. The pollen zones are indicated and correspond to Figure 6.1.*

probably represents deposition from around 5100-5300 cal. yrs BP. $\delta^{13}C$ values are between –26.6‰ and –27.1‰, with an overall trend towards more negative values. C/N lie within relatively tight bounds of 18.6 to 25.1. Although C/N are comparable with saltmarsh sampled in the contemporary environment, however $\delta^{13}C$ are more negative in the core record, with a shift by 10‰.

Zone 2 (372-386 cm)

Three centimetres of herbaceous fen has been sampled in the Little Cheyne Court core, and its pollen indicates the presence of species such as *Quercus robur*, *Corylus avellana* (likely to have been growing some distance from the site) and *Betula*, as well as Cyperaceae and Poaceae (see Figure 6.1). The radiocarbon date of 4549-4861 cal. yrs BP above the saltmarsh section has a $\delta^{13}C$ value of –27.9‰, which fits into the general pattern of the $\delta^{13}C$ becoming more negative. The sampled fen has $\delta^{13}C$ of *c.* –28.3‰ and C/N of *c.* 40.

Zone 3 (352-372 cm)

In Zone 3 there is an increase in the abundance of Pteropsida, although this appears to be having little impact on the $\delta^{13}C$ and C/N of the peat formed. This section has more negative $\delta^{13}C$ of –28.5 ± 0.3‰, and C/N of 38.2 ± 1.2. The transition into a poor fen community is characterised by an increase in $\delta^{13}C$ to around –28.8‰ and a decrease in C/N to 20.8.

Zone 4 (338-352 cm)

This portion of the Little Cheyne Court core sees an increase in the proportion of *Myrica gale* and a reduction in the abundance of *Sphagnum* and Cyperaceae and Poaceae. This zone sees a change in the relatively stable $\delta^{13}C$ of around -28.1‰ gradually decrease to around -29.3‰. C/N remains fairly stable at around 30.

Zone 5 (306-338 cm)

The acidophilic bog, according to the pollen record (Waller *et al.*, 1999) contains Sphagnum, *Calluna vulgaris*, while species such as *Corylus avellana* and *Alnus glutinosa* (likely to be growing some distance from the acidophilic bog) are represented in the pollen record. The second radiocarbon date from the Little Cheyne

Court core (4263-3981 cal. yrs BP) has a $\delta^{13}C$ of –26.9‰. In Zone 5 there is an overall increase in $\delta^{13}C$ from –28.5‰ to –27.2‰. At around 3850 cal. yrs BP there is a peak in $\delta^{13}C$, with a maximum value of –25.7‰. These apparent peaks (including the poor fen/bog transition) coincide with higher abundance of *Sphagna* in the pollen record. C/N for raised bog is usually between 40-50, with no obvious trend.

Zone 6 (278-306 cm)

Zone 6 sees a change from bog to Cyperaceae-dominated environments, with high pollen abundance of *Eriophorum*. The transition shows a continuation of the pattern shown in the acidophilic bog, with an increase in the $\delta^{13}C$ to a final maximum value of –25.3‰ at around 3000 cal. yrs BP. The $\delta^{13}C$ then decreases dramatically and consistently for the next 200 years, before beginning to increase to around –27.5‰ and to the development of raised bog conditions. C/N fluctuate around 50 for the Cyperaceae-dominated environment, before falling to around 30 at the time of the Cyperaceae-dominated/ombrotrophic bog transition. A radiocarbon date of 2745-2358 cal. yrs BP (Waller *et al.*, 1999) has provided a $\delta^{13}C$ value of –27.4‰.

Zone 7 (228-278 cm)

The ombrotrophic bog is characterised by the continued presence of Cyperaceae and Poaceae, and the dominance of species such as *Calluna vulgaris*, *Sphagnum.* The earliest part of the raised bog sequence (until 1700 cal. yrs BP) is typified by sharp fluctuations in $\delta^{13}C$ and C/N. Overall there is a trend towards more negative $\delta^{13}C$ s (from –26.1‰ to –27.7‰) and more negative C/N (from over 80 to below 50). The most recent sequence of raised bog, post-1500 cal. yrs BP has much more stable $\delta^{13}C$ geochemistry, fluctuating around –27.0‰. C/N is centred on 50, with fluctuations generally less than 15.

6.3 Hope Farm

The Hope Farm core peat sequence is shorter than at Little Cheyne Court, but still records over 3000 years of vegetation change. The contiguous sampling strategy has provided 97 samples, covering five vegetation communities (saltmarsh, herbaceous fen, alder-dominated carr, Cyperaceae-dominated and *Myrica*-dominated). Figure

6.4 compares the pollen record (from Waller *et al.*, 1999) to the $\delta^{13}C$ and C/N data. Figures 6.5 and 6.6 illustrate the $\delta^{13}C$ and C/N of the peat of Hope Farm from 1500-5300 cal. years BP. Similarly to the Little Cheyne peat sequence, the zonation is based on that of Waller *et al.* 1999, and uses the palynology to determine vegetation communities. This allows comparison between $\delta^{13}C$ and C/N with the vegetation communities from which they have been sampled.

6.3.1 Hope Farm core $\delta^{13}C$ and C/N

Zone 1 (below 299 cm)

Peat forming communities at the Hope Farm site apparently begin with saltmarsh communities, dominated by Chenopodiaceae, Cyperaceae and Poaceae around 5200 cal. yrs BP (Waller *et al.*, 1999). The saltmarsh $\delta^{13}C$ decreases from –26.3‰ to –27.2‰ up the core, while the C/N remains low at around 12.

Zone 2 (290-299 cm)

Pollen suggests a gradual shift away from marine and brackish environments, with saltmarsh plants replaced by fen plants, with higher pollen values of Cyperaceae and Poaceae (see Figure 6.4). The boundary between saltmarsh and fen carr has a $\delta^{13}C$ of –27.5‰ from the radiocarbon date of 1876-1629 cal. yrs BP. This negative trend continues into the fen carr community, with falling as low as –28.9‰. C/N show a slight increase, to around 20, as organic carbon concentrations increase.

Zone 3 (250-290 cm)

Zone 3 sees the establishment of an alder-dominated carr communities and is characterised by higher pollen values of *Alnus glutinosa*. This initial domination has $\delta^{13}C$ fluctuating around –28.7‰ and C/N remain relatively stable around 20. Immediately below the radiocarbon date of 3827-3569 cal. yrs BP (with a $\delta^{13}C$ value of –27.5‰) the alder pollen values decrease slightly. In this second phase both the $\delta^{13}C$ and C/N become more variable, and overall increase slightly.

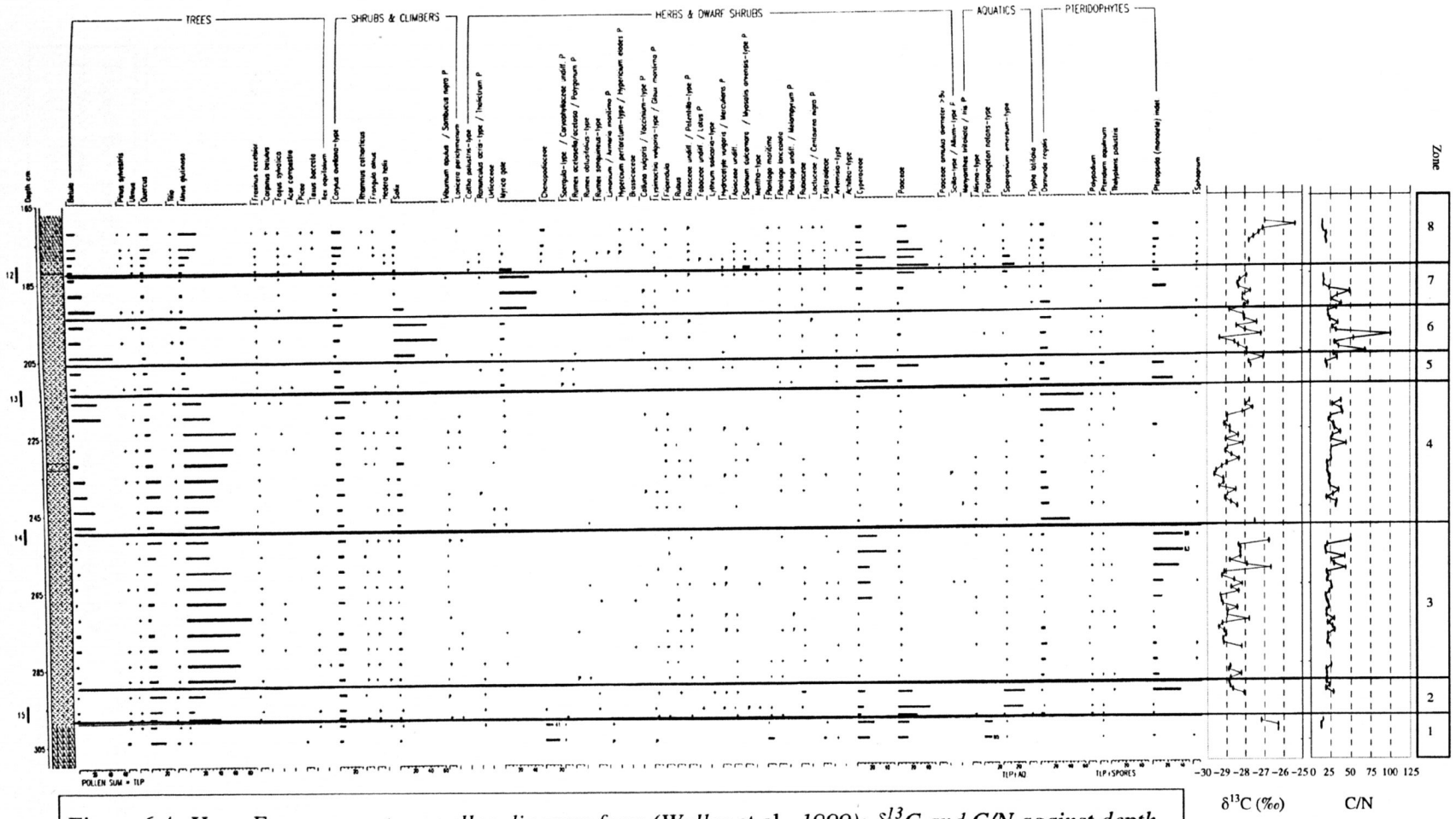


Figure 6.4: *Hope Farm percentage pollen diagram from (Waller* et al., *1999); $\delta^{13}C$ and C/N against depth. The + and P symbols indicate <1% total land pollen (TLP). The 8 pollen zones are indicated.*

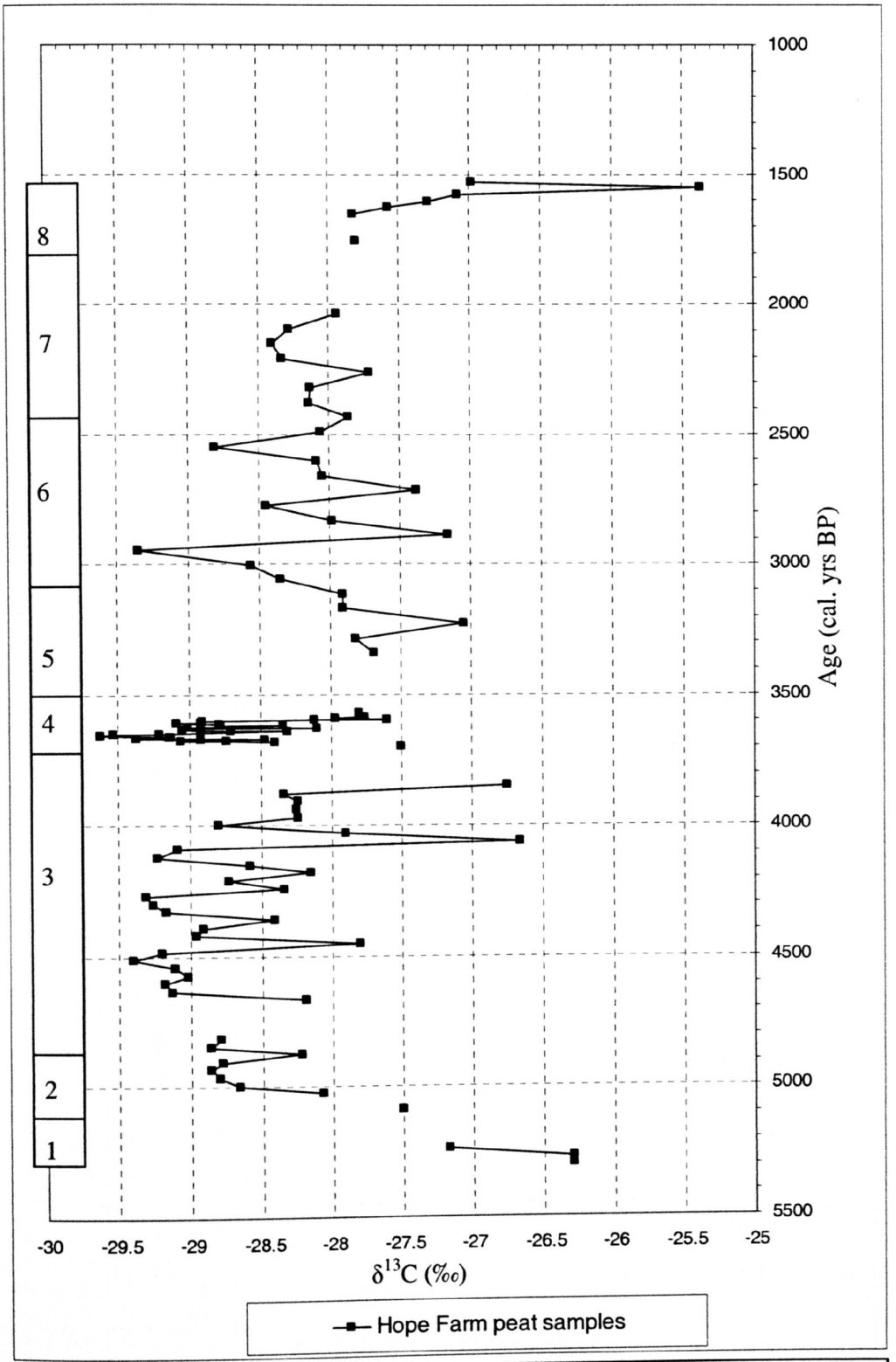


Figure 6.5: *Change in $\delta^{13}C$ through the Hope Farm core through time. The pollen zones are indicated and correspond to Figure 6.4.*

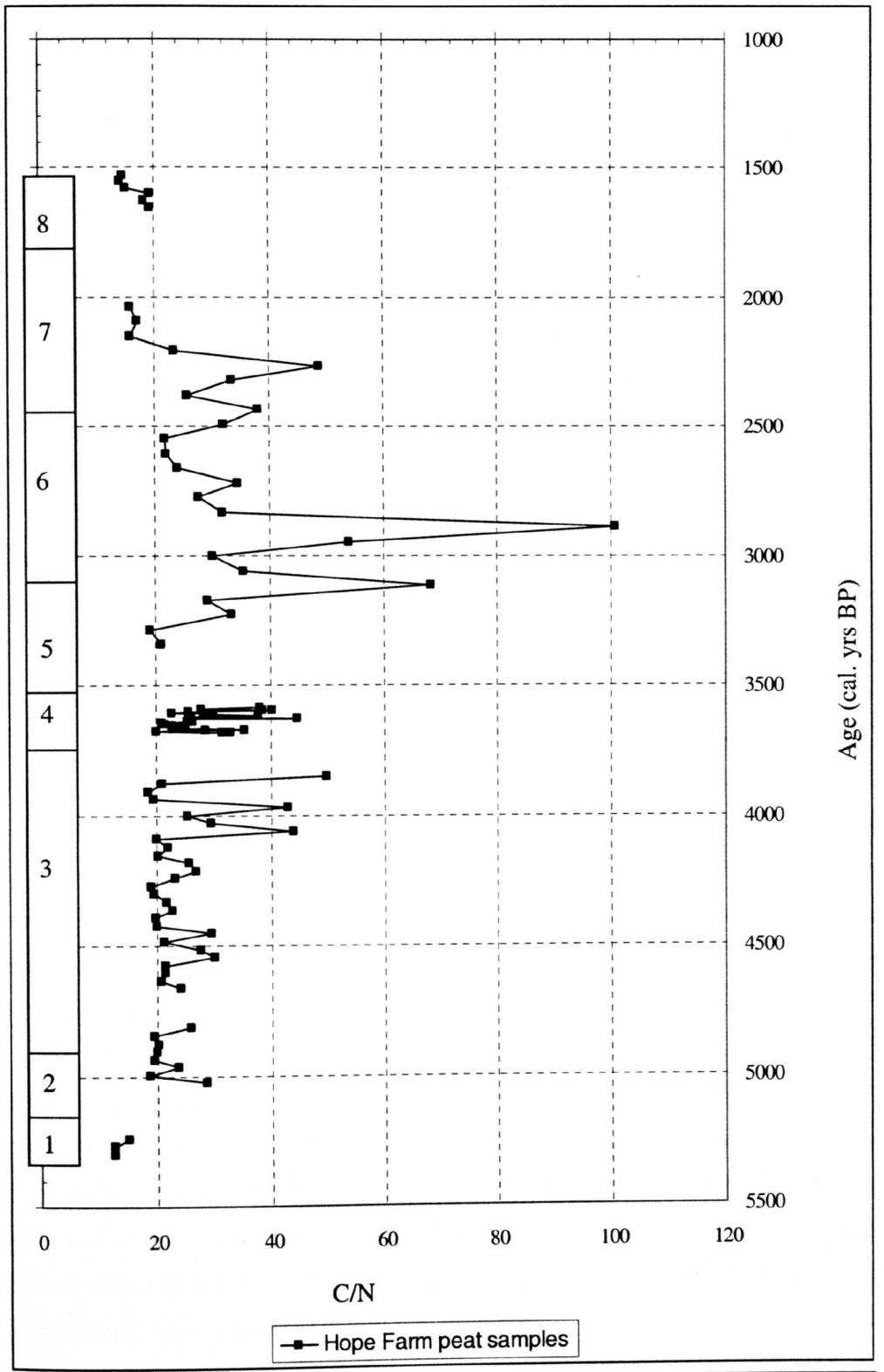


Figure 6.6: *Change in C/N through the Hope Farm core through time. The pollen zones are indicated and correspond to Figure 6.4.*

Zone 4 (214-250 cm)

Zone 4 represents the continued devleopment of alder-dominated carr before a transition to a more 'open' environment. The radiocarbon dates from above and below this zone imply that there was rapid deposition at this time. The $\delta^{13}C$ data is variable within Zone 4 generally between –28.0‰ and –29.7‰. Towards the top of Zone 4 the $\delta^{13}C$ increases from –29.0‰ to –27.8‰ and remains at this value. The C/N initially remains steady, close to values of 20. Between 230 and 214 cms it becomes more variable, with values from 20 to 30.

Zone 5 (206-214 cm)

According to the pollen record, *A. glutinosa* reduces dramatically at 3681-3459 cal. yrs BP. An opening in the carr environment persists to allows a Cyperaceae-dominated community to exist from around 3400-3200 cal. yrs BP. This is typified by high $\delta^{13}C$ (–27.8 to –27.1‰), and C/N of 19-33.

Zone 6 (189-206 cm)

By around 3100 cal. yrs BP the pollen shows that a fen carr community returns, with domination by *Salix* (Waller *et al.*, 1999). This part of the core is likely to be similar to the contemporary environment found at Old House Farm. $\delta^{13}C$ fluctuates around –28.0‰, by ± 0.8‰, while the C/N are hugely variable, from 21 to 101. $\delta^{13}C$ are between 1 - 2.5‰ more negative in the core record than at Old House Farm. The increases in C/N are probably related to increases in the occurrence of wood and stem material found in the core.

Zone 7 (183-189cm)

Zone 7 sees a change in the pollen assemblage, with an increase in *Myrica gale* and a decrease in *Salix* spp. This appears not to have significantly affected the $\delta^{13}C$ record, with $\delta^{13}C$ continuing around –28.0‰ although the variability around this value is generally less than 0.5‰. The C/N are also variable, from 15 to 48, however the overall trend is towards lower values.

Zone 8 (above 183 cm)

The final vegetation community of the main marsh peat found at Hope Farm is described by Waller *et al.* (1999) as herbaceous fen. The pollen record suggests that there was an increase in the pollen of *Alnus glutinosa* and reduction of *Myrica gale.* The increase in Chenopodiceae and polyhabous diatoms (see Waller *et al.*, 1999) indicates that marine inundation occurred during this stage. $\delta^{13}C$ support this theory, with rapidly increasing $\delta^{13}C$, from –27.8‰ with one value as high as –25.4‰. C/N are also relatively low (14-19), and are more comparable with the C/N found within the saltmarsh at Hope Farm.

6.4 Comparison between Little Cheyne Court and Hope Farm $\delta^{13}C$ and C/N

Relating changes between the geochemical data from Little Cheyne Court and Hope Farm to vegetation response to effects such as changes in local coastal conditions can be made with more confidence if the timing of these events in contemporaneous. The age models for the Little Cheyne Court and Hope Farm cores are based on the radiocarbon dates from Waller *et al.* 1999, assuming a constant rate of sedimentation between radiocarbon dated samples. Little Cheyne Court had a consistent rate of sedimentation, varying between 0.36 and 0.45 mm/year, wheras Hope Farm had a sedimentation rate varying from 0.18 to 2.50 mm/year. If there is a wider-scale process, such as a change in local or regional climate then it is thought that this could impact on the vegetation communities found in the Little Cheyne Court and Hope Farm cores. The investigated communities are not the same in the two cores, however any influence is likely to lead to a change in the isotope geochemistry in a similar way, even though not to the same magnitude. Therefore contemporaneous patterns of change will be investigated by comparing the two cores, rather than attempting to quantify the influence or the effect on the vegetation communities.

Figures 6.7 and 6.8 compare the $\delta^{13}C$ and C/N data of Little Cheyne Court and Hope Farm with each other, and include their geochemical zonation. Little Cheyne Court has four zones based on the $\delta^{13}C$ of the preserved peat material. From *c.* 5300 to *c.* 4200 cal. yrs BP the $\delta^{13}C$ decreases from –26.7‰ to –29.3‰ (LCC 1). This is followed by an increase to –25.5‰ at *c.* 2990 cal. yrs BP (LCC 2). In LCC 3 (*c.* 2990 to *c.* 2390 cal. yrs BP) the $\delta^{13}C$ record remains relatively stable, fluctuating

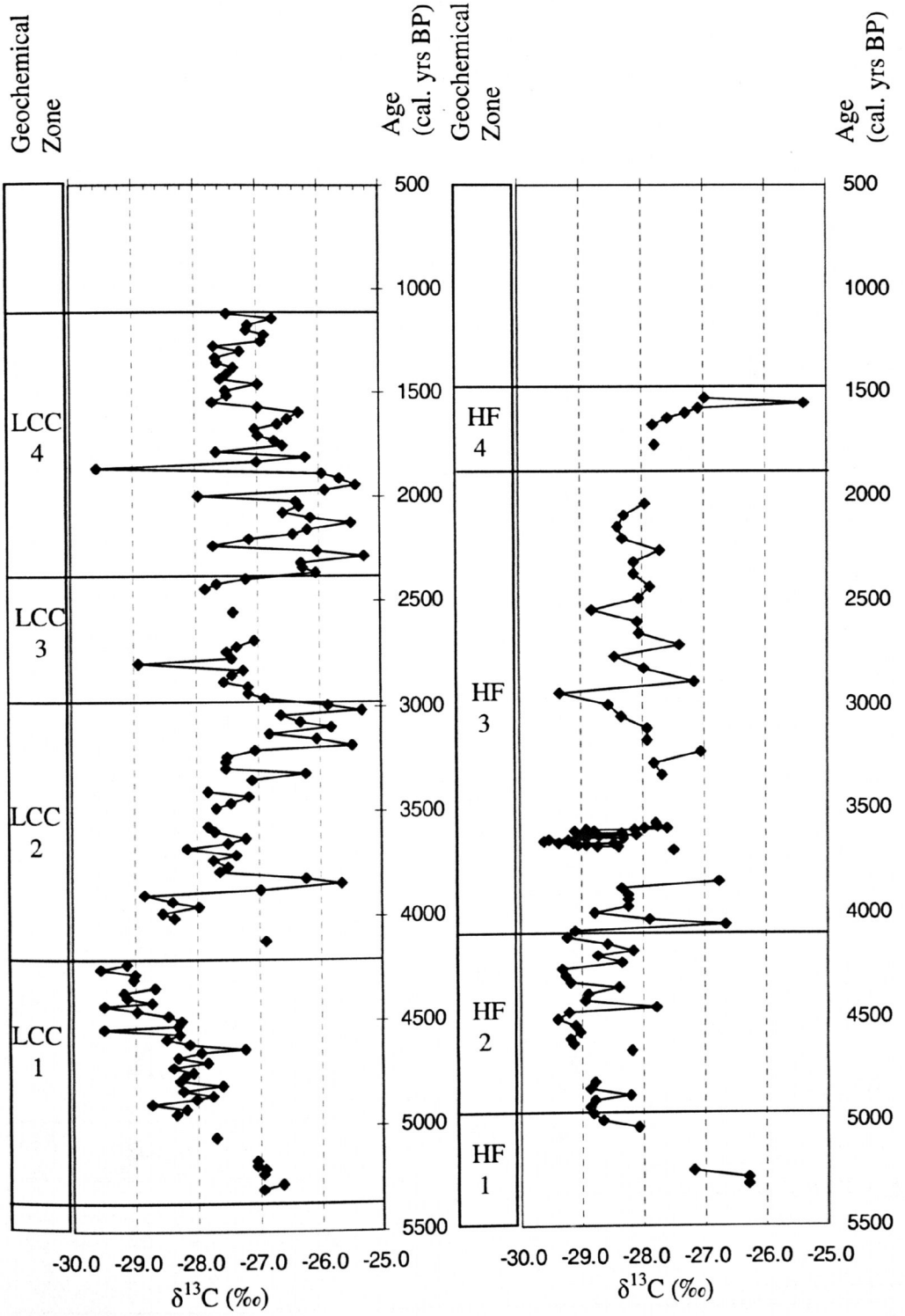


Figure 6.7: *Comparison between the $\delta^{13}C$ of Little Cheyne Court (left) and Hope Farm (right) through time.*

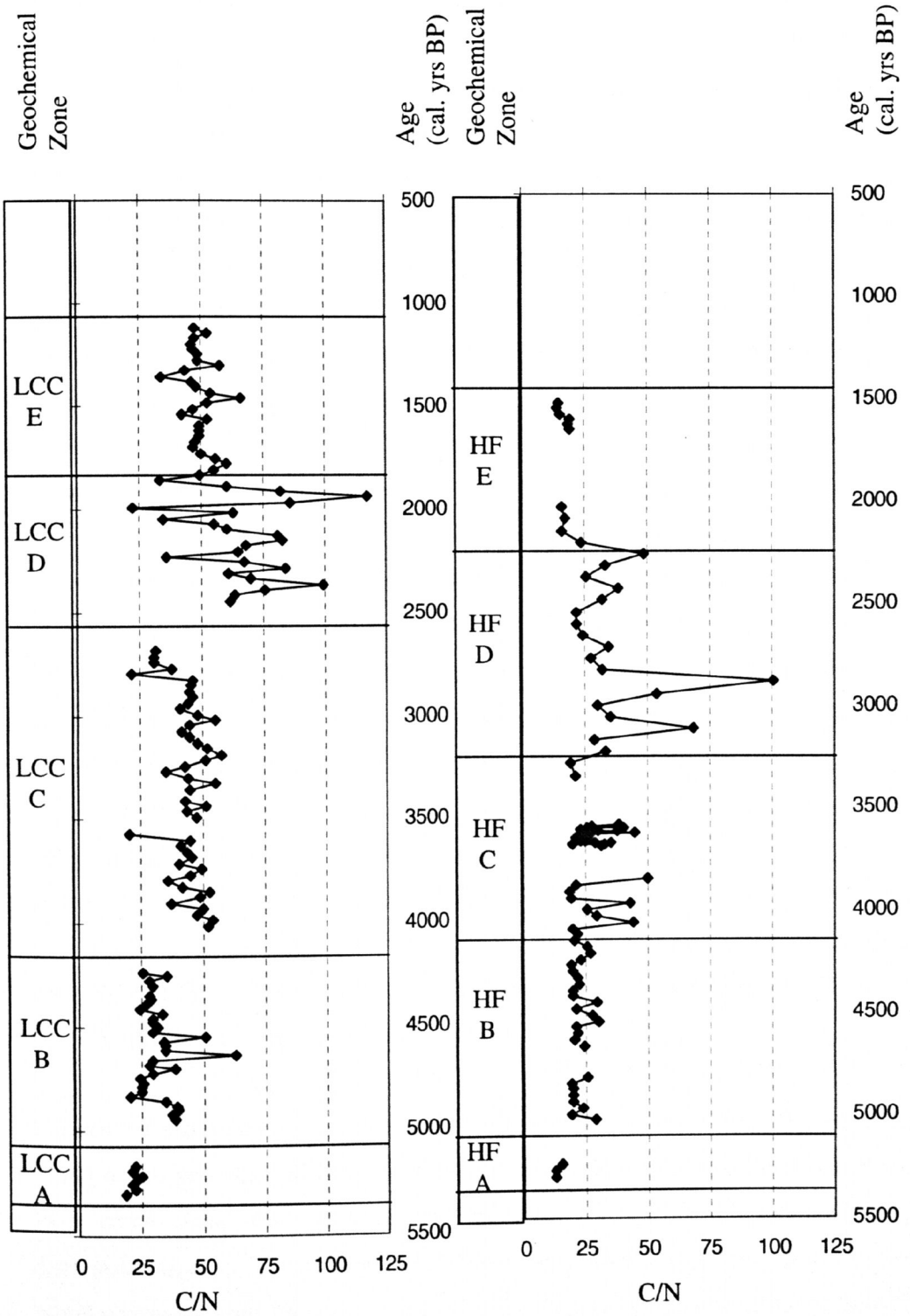


Figure 6.8: *Comparison between the C/N of Little Cheyne Court (left) and Hope Farm (right) through time.*

between –27.0‰ and –28.0‰. From *c.* 2390 to *c.* 1120 cal. yrs BP (LCC 4) the $\delta^{13}C$ of the peat material fluctuates from –29.6‰ to –25.3‰. The Hope Farm core also has four $\delta^{13}C$ zones, however they do not correlate closely to the Little Cheyne Court zonation. A similar decline occurs in HF 1 as LCC 1, from –26.3‰ to –28.8‰, but this occurs over a much shorter time period, from *c.* 5300 to *c.* 4960 cal. yrs BP. The $\delta^{13}C$ record of HF 2 (*c.* 4960 to *c.* 4120 cal. yrs BP) indicates fluctuations from –27.8‰ to –28.2‰. In HF 3 (*c.* 4120 and *c.* 2000 cal. yrs BP) the fluctuations increase in magnitude, from –26.6‰ to -29.6‰. The final stage, HF 4 reveals a continued increase in $\delta^{13}C$ from *c.* –28.0‰ to *c.* –27.0‰ up until the end of peat deposition at *c.* 1530 cal. yrs BP.

There is closer correlation between the Little Cheyne Court and Hope Farm cores based on zonation the C/N record of the preserved sampled peat. Each of the two cores have five separate geochemical zones. In LCC A and HF A (from *c.* 5300 to *c.* 5100 cal. yrs BP) the C/N remains low (18 – 25 for LCC A and 12 – 15 for HF A). This is followed by an increase in C/N for each site, with LCC B generally having C/N between 25 – 40, and HF B having C/N between 19 – 30, which represents deposition from *c.* 5100 to *c.* 4150 cal. yrs BP. The pattern found in LCC C (*c.* 4150 to *c.* 2550 cal. yrs BP) is similar to that found in HF C (*c.* 4150 to *c.* 3280 cal. yrs BP). During this time C/N increases once again, generally from 35 – 60 for LCC C and 19 – 43 for HF *C.* In LCC D (*c.* 2550 to *c.* 1780 cal. yrs BP) and HF D (*c.* 3280 to *c.* 2200 cal. yrs BP) the C/N is much more variable, from 21 – 117. In the final zone, the C/N for LCC E (*c.* 1780 to *c.* 1120 cal. yrs BP) fluctuates around 50, while in HF E (*c.* 2200 to *c.* 1530) the C/N declines to 14 – 19.

Figures 6.9 and 6.10 compare the pollen zones and major pollen taxa (Waller *et al.*, 1999) to the geochemical zones identified from the Little Cheyne Court and Hope Farm cores. Using $\delta^{13}C$ and C/N zonation alone it is not possible to individually distinguish changes in the pollen assemblage, and thus the vegetation communities found within the core. However, the $\delta^{13}C$ and C/N zones do tend to match with each other fairly closely, indicating that both $\delta^{13}C$ and C/N should be used in combination for reconstructing palaeoenvironments.

Estimated Age (cal. yrs BP)	**Pollen Zone**	**Major Taxa**	**$\delta^{13}C$ Zone**	**C/N Zone**
5190 – 5300	1	Cyperaceae, Poaceae, Chenopodiaceae	LCC 1	LCC A
4855 – 5190	2	Poaceae, *Quercus*, Cyperaceae, *Corylus avellana*-type	LCC 1	LCC A
4455 – 4855	3	Pteropsida (monolete) indet., *Betula*, *Sphagnum*	LCC 1	LCC A
4165 – 4455	4	*Betula, Corylus avellana*-type, *Myrica gale*	LCC 1/ LCC 2	LCC A
3270 – 4165	5	*Sphagnum, Corylus avellana*-type, *Calluna vulgaris*, *Alnus glutinosa*	LCC 2	LCC B
2550 – 3270	6	*Corylus avellana*-type, Cyperaceae, Poaceae	LCC 2/ LCC 3	LCC C
1195 – 2550	7	*Sphagnum*, Poaceae, Cyperaceae	LCC 3/ LCC 4	LCC D/ LCC E

Figure 6.9: *Comparison between the pollen zones, major taxa and geochemical zones for the Little Cheyne Court core.*

Estimated Age (cal. yrs BP)	**Pollen Zone**	**Major Taxa**	**$\delta^{13}C$ Zone**	**C/N Zone**
4600 – 5300	1	*Potamageton natans*-type, Chenopodiaceae, Cyperaceae, Poaceae	HF 1/ HF 2	HF A/ HF B
4545 – 4600	2	Poaceae, *Sparganium emersum*-type, *Alnus glutinosa, Quercus*	HF 2	HF B
3665 – 4545	3	*Alnus glutinosa,* Cyperaceae, Pteropsida (monolete) indet.	HF 2/ HF 3	HF B/ HF C
3190 – 3665	4	*Alnus glutinosa, Betula, Quercus, Osmunda regalis*	HF 3	HF C/ HF D
3000 – 3190	5	Cyperaceae, Poaceae, Pteropsida (monolete) indet.	HF 3	HF D
2035 – 3000	6	*Salix, Betula, Osmunda regalis*	HF 3	HF D/ HF E
1700 – 2035	7	*Myrica gale, Betula*	HF 3/ HF 4	HF E
1530 – 1700	8	Poaceae, Cyperaceae, *Alnus glutinosa*	HF 4	HF E

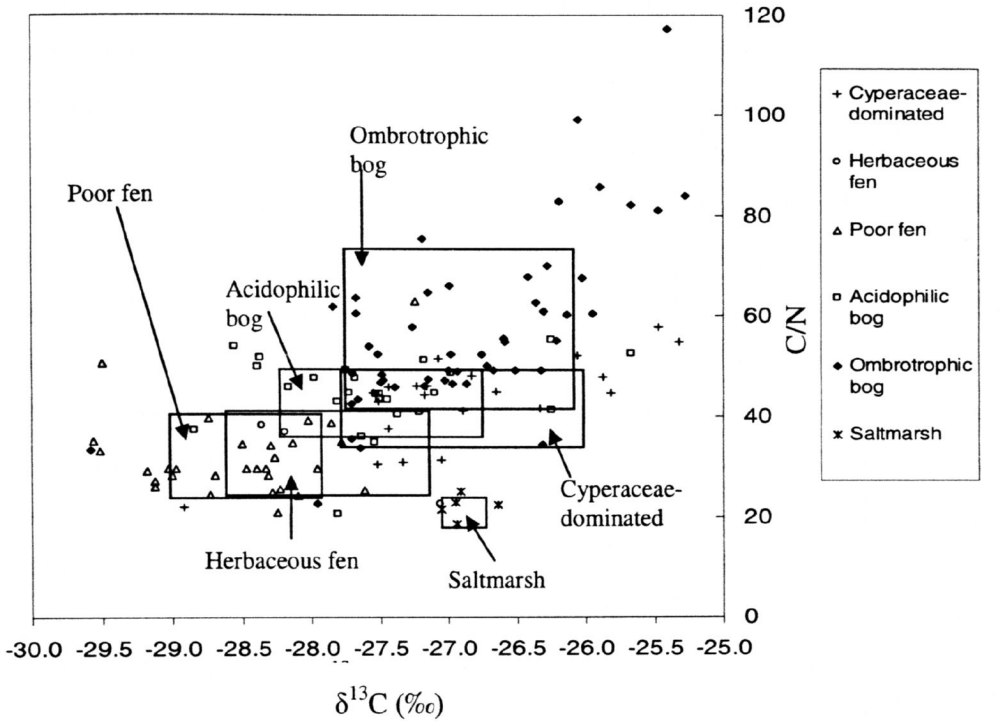
Figure 6.10 *Comparison between the pollen zones, major taxa and geochemical zones for the Hope Farm core.*

6.5 $\delta^{13}C$ and C/N of vegetation communities in Romney Marsh

The 234 bulk peat samples from seven vegetation communities provide the opportunity to determine whether vegetation communities have specific $\delta^{13}C$ and C/N. Figure 6.11 compares $\delta^{13}C$ and C/N for the vegetation communities inferred from the pollen data from the Hope Farm and Little Cheyne Court cores. The graphs show that the only vegetation community that can be distinguished from the others is saltmarsh. The saltmarsh communities of Little Cheyne Court and Hope Farm generally have relatively high $\delta^{13}C$ (–26.8‰ to –27.1‰ and –26.1‰ to –27.1‰ respectively) and generally low C/N (20 to 24 for Little Cheyne Court and 12 to 15 for Hope Farm).

Although the other sampled vegetation communities do not have distinct $\delta^{13}C$ and C/N, certain generalisations can be made. In the Little Cheyne Court core there is a gradational pattern of increasing $\delta^{13}C$ and C/N related to the vegetation succession found in the core. Poor fen has the most negative $\delta^{13}C$ and lowest C/N (–27.9‰ to –29.1‰ and 23 to 40 respectively). Herbaceous fen has similar C/N, but a slightly less negative $\delta^{13}C$ of –27.2‰ to –28.6‰). The Cyperaceae-dominated and acidophilic bog communities both have an increased C/N ratio and $\delta^{13}C$ compared to the fen communities. The Cyperaceae-dominated vegetation has $\delta^{13}C$ from –26.1‰ to –27.7‰ and C/N from 34 to 52, while acidophilic bog has $\delta^{13}C$ from –26.8‰ to –28.2‰ and C/N from 37 to 52. The most recently deposited sediment, deposited in ombrotrophic bog environments, has the least negative $\delta^{13}C$ (–26.1‰ to –27.7‰) and highest C/N (40 to 75).

In the Hope Farm core it is not possible to distinguish between the 'woody' vegetation communities sampled in this study. Alder-dominated carr, *Myrica gale*-dominated and fen carr sediments all have similar C/N ratios, within the bounds of 15 to 40. The $\delta^{13}C$ of the sediments are also generally between –27.7‰ and –29.2‰. *Myrica gale*-dominated sediments tend to be at the least negative end of this scale, with values from –27.9‰ to –28.3‰. Cyperaceae-dominated communities tend to have much less negative $\delta^{13}C$ compared to the woody components, with values from –27.2‰ to –28.0‰, however the C/N is indistinguishable from the 'woody' vegetation communities.



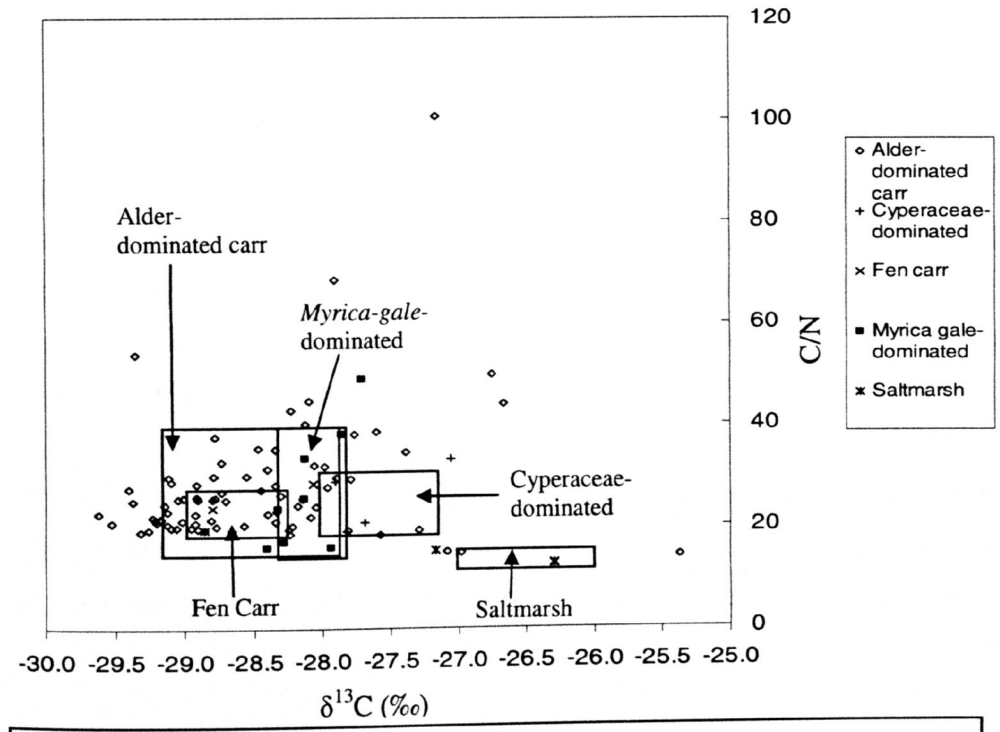


Figure 6.11: Comparison between the $\delta^{13}C$ and C/N of the vegetation communities found in the Little Cheyne Court (top) and Hope Farm (bottom) cores. Boxes indicate mean ± standard deviation.

Saltmarsh and Cyperaceae-dominated communities are the only vegetation communities which are found in both cores. Comparing the Cyperaceae-dominated communities of Little Cheyne Court and Hope Farm is problematic due to the composition of the vegetation, and are likely to be very different. This is reflected in the isotope geochemistry, since the Cyperaceae-dominated vegetation sampled at Little Cheyne Courth have much less negative $\delta^{13}C$ (–26.1‰ to –27.7‰) than Hope Farm (–27.2‰ to –28.0‰) and the C/N ratios are also much higher (34 to 52 at Little Cheyne Court compared to 19 to 32 at Hope Farm). This study highlights the need for careful description of vegetation communities and the potential for using $\delta^{13}C$ and C/N ratios as a way of determining the nature of the environment. Saltmarsh communities appear to have more consistent $\delta^{13}C$ in both cores, ranging from –26.8‰ to 27.1‰ at Little Cheyne Court and –26.1‰ to –27.1‰ at Hope Farm. The C/N ratios are also similar from 20 to 24 at Little Cheyne Court and 12 to 14 at Hope Farm. The slight difference between the two sites is also likely to be due to the low percentage of carbon found in the sediment (thus a small change in the %C will cause large changes in the C/N ratio).

6.6 $\delta^{13}C$ and C/N of other UK historical sites

There have been a number of investigations in the UK which have examined $\delta^{13}C$ and C/N of peat material and compared it to the inferred vegetation community (e.g., Andrews *et al.*, 2000; Wilson *et al.*, 2005a, b; Allen *et al.*, 2007). Other investigations of vegetation communities have also produced radiocarbon dated peat samples. As part of the radiocarbon dating process the $\delta^{13}C$ ratio is also usually measured, and thus a range of vegetation communities can be explored across the UK using these $\delta^{13}C$ produced as part of the dating (e.g., Anderson, 1998; Charman *et al.*, 1999; de la Vega Leinart *et al.*, 2000; Chiverell, 2001; Anderson, 2002; Bunting and Tipping, 2004; Hughes and Barber, 2004; Selby, 2004; Caseldine and Gearey, 2005; Langdon and Barber, 2005; O'Brien *et al.*, 2005).

Figure 6.12 compares $\delta^{13}C$ of ancient peat for five vegetation categories found within the Hope Farm and Little Cheyne Court cores to other UK data sets. The data shows clear similarities between the other UK sites and data collected in this study. Although there is a range in the $\delta^{13}C$ values, alder-dominated carr and herbaceous

fen communities tend to have more negative $\delta^{13}C$ than bog and Cyperaceae communities. The range in $\delta^{13}C$ of saltmarsh sediments is much larger in other U.K sites, however this is likely to be related to varying quantities of marine plankton in the sediments.

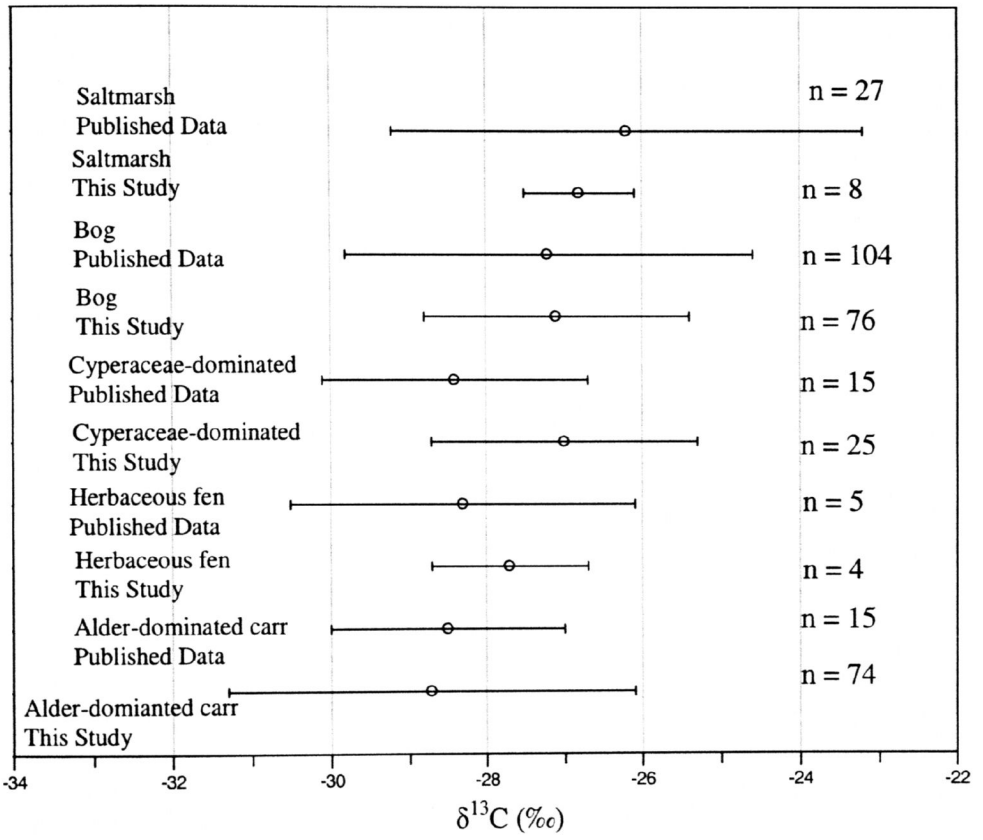


Figure 6.12: *Comparison between the $\delta^{13}C$ of published data and this study for the vegetation communities found within the Hope Farm and Little Cheyne Court cores.*

As has been illustrated in Chapter 3.5 vegetation communities can be very variable in their nature. This means that although it is possible to state that some vegetation communities will be similar in their composition, they will not be the same. As a result there is a large degree of variability of $\delta^{13}C$ within each vegetation community. Using $\delta^{13}C$ and C/N without any other palaeoenvironmental information, it is not possible to reconstruct the vegetation community with any degree of confidence.

6.7 Conclusions

This chapter has examined $\delta^{13}C$ and C/N of vegetation communities found within the main marsh peat layer of two cores from Hope Farm and Little Cheyne Court. Comparison to equivalent contemporary environments has shown a trend towards more negative $\delta^{13}C$ in the record. It has also revealed that there is a range of $\delta^{13}C$ and C/N values for vegetation communities, both within and between cores, and to other investigated sites in the UK. The following chapter will examine in detail possible reasons for changes in the $\delta^{13}C$ and C/N, in terms of past climate and natural variability within vegetation communities.

Chapter 7: Assessing the use of $\delta^{13}C$ and C/N in palaeoenvironmental reconstruction

7.1 Introduction

The purpose of this chapter is to evaluate the use of $\delta^{13}C$ and C/N as a palaeoenvironmental tool for reconstructing palaeoenvironmental change in the former Romney Marsh coastal wetlands. This is performed by examining the role of the changing atmospheric $\delta^{13}C$ ratios, environmental stresses and post-depositional changes on the final $\delta^{13}C$ and C/N ratios of the peat samples analysed in Section 2.5. It directly compares the contemporary record of the Romney Marsh sites to the vegetation communities in the fossil core record. It also compares the regional records of Romney Marsh and Norfolk to those from the UK, and to known climatic changes during the mid to late Holocene.

7.2 Source of carbon

Any change in the $\delta^{13}C$ of atmospheric CO_2 for terrestrial plants will lead to a change in the final soil $\delta^{13}C$. The contemporary plant and soil material $\delta^{13}C$ in this study have been converted so that they are comparable with pre-Industrial atmospheric $\delta^{13}C$ ratios (McCarroll and Loader, 2004) (see Chapter 2.5.1). This in turn makes them comparable to the fossil soils. The main assumption in this research concerning the source of carbon is that mid to late Holocene levels of atmospheric $\delta^{13}C$ have remained constant, at a value of around –6.4‰ (Francey *et al.*, 1999). Measurements from air trapped in ice cores from Byrd Station, Antarctica, have shown that early Holocene atmospheric $\delta^{13}C$ were around –6.8‰, and increased to –6.5 ± 0.12‰ at pre-Industrial times (Leuenberger *et al.*, 1992). $\delta^{13}C$ values, using modelled projections at Taylor Dome, also in Antarctica, showed there was a general increase from –6.3‰ to -6.5‰ from 8000 to 1000 cal. yr BP (Indermühle *et al.*, 1999). Examining the $\delta^{13}C$ of CO_2 within the air trapped in the ice cores at Taylor Dome shows that from 5200 to 2200 cal. yrs BP (roughly equivalent to the investigated period in the Hope Farm and Little Cheyne Court cores) this shift was from around –6.5‰ to –6.6‰ (Indemühle *et al.*, 1999). Generally therefore, for the mid to late Holocene, the $\delta^{13}C$ of the atmosphere has only decreased by around 0.1 to 0.2‰

which is within the 1 and 2 standard deviations error of the data, and therefore can be ignored in the following discussion of the Hope Farm and Little Cheyne Court cores.

7.3 Environmental stresses

It has been shown (Chapter 2.5.2) that local, regional and global environmental changes can lead to changes in $\delta^{13}C$ of both plant and soil material. Changes in the $\delta^{13}C$ and C/N of the peat found at Hope Farm and Little Cheyne Court may also result from environmental processes operating over these scales. This can be tested by comparing known climatic events, or other environmental stresses, to the Romney Marsh cores. This must be done while keeping in mind the other factors which influence the $\delta^{13}C$ and C/N of the peat, including changes in vegetation composition (e.g., through seral succession), post-depositional changes to the sedimentary record and changes in relative sea-level and the influence this has on the height of the water table. Changes in the $\delta^{13}C$ and C/N record will not necessarily be related to regionally driven climate change, but do represent changes in local coastal conditions in south-east England. More research, on a wider scale, would need to be undertaken before firmer conclusions could be made.

7.3.1 Little Cheyne Court

The age model for Little Cheyne Court is adapted from Waller *et al.* (1999), which assumes a constant sedimentation rate between calibrated radiocarbon dated peat samples. In the case of Little Cheyne Court the sedimentation rate is 0.36 to 0.45 mm/year (1 cm per 22 – 28 years). Since the sedimentation rate appears to have remained relatively constant, spectral analysis can be carried out with confidence, using changes in $\delta^{13}C$ to determine whether any cyclical changes can be identified.

Ombrotrophic bogs are known to be very sensitive to changes in water availability, and particularly to precipitation (e.g., Charman *et al.*, 1999; Chiverell, 2001; Hughes and Barber, 2004; Blundell and Barber, 2005; Caseldine and Gearey, 2005; Langdon and Barber, 2005; Schoning *et al.*, 2005). In the case of Romney Marsh this mainly relates to changes in the height of the water table and secondly to precipitation. Little Cheyne Court The main climatic shift recorded in previous studies of Romney Marsh occurs at the Sub-boreal/Sub-atlantic chronozone boundary (Waller *et al.*, 1999),

dated to 2800-2710 cal. yrs BP (Kilian *et al.*, 1995; van Geel *et al.*, 1996). This represented a general shift towards wetter conditions. This shift has been identified by multi-proxy data (such as the changing abundance of species of testate amoebae, which are sensitive to changes in water availability (Woodland *et al.*, 1998)) from ombrotrophic bogs across the UK.

Cycles in the Little Cheyne Court $\delta^{13}C$ record

The rate of sediment deposition at Little Cheyne Court has remained relatively constant throughout the period of peat formation. For this reason it is possible to apply spectral analysis to the $\delta^{13}C$ record to explore the evidence for cycles in the isotope and C/N data. Figure 7.1 shows that two cycles exist at the greater than 95% confidence limits, and one of them at greater than 99% confidence. These cycles have periodicities of 1005 and 1675 years respectively. The high degree of certainty that these are statistically significant cycles suggeststhat they represent a forcing on the $\delta^{13}C$ of the deposited material (Figure 7.2).

The high-resolution sampling of the Little Cheyne Court cores allows me to test the hypothesis that the 1005 and 1675 year cycles represent cyclical changes in local coastal conditions. Langdon *et al.* (2003) examined a 7500-year core from Temple Moss, an ombrotrophic bog in south-east Scotland, to examine whether raised bog and poor fen environments reacted in a similar way to precipitation changes. Evidence for an 1100-year cycle of climate was found in this record. Nearby Walton Moss also revealed a similar cyclicity (Hughes *et al.*, 2000).

Influences on the $\delta^{13}C$ at Little Cheyne Court

Figure 7.2 shows possible various phases of change identified in the Little Cheyne Court, with a particular emphasis on correlating this to wider regional climate events. The phases represent shifts *towards* higher water availability, rather than times of high water availability. These shifts (4800-4400, 2800-2400 and 1900-1400 cal. yrs BP) closely correlate with various observations from ombrotrophic bogs across north-west Europe of increased precipitation (Aaby, 1976; van Geel *et al.*, 1996; Ellis and Tallis, 2000; Hughes, *et al.*, 2000; Barber *et al.*, 2003; Barber *et al*, 2004; Langdon *et al.*, 2005).

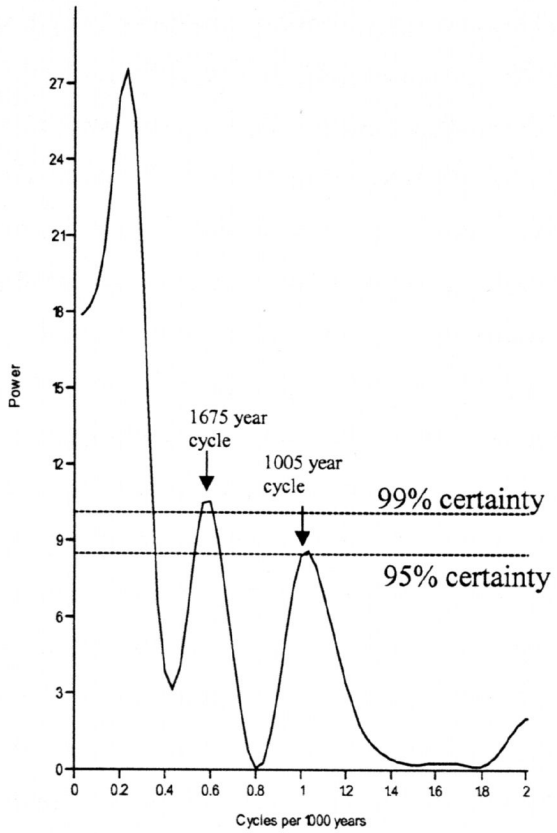


Figure 7.1: *Spectral analysis from Little Cheyne Court (excluding saltmarsh). The two dotted lines indicate 95% and 99% statistical significance*

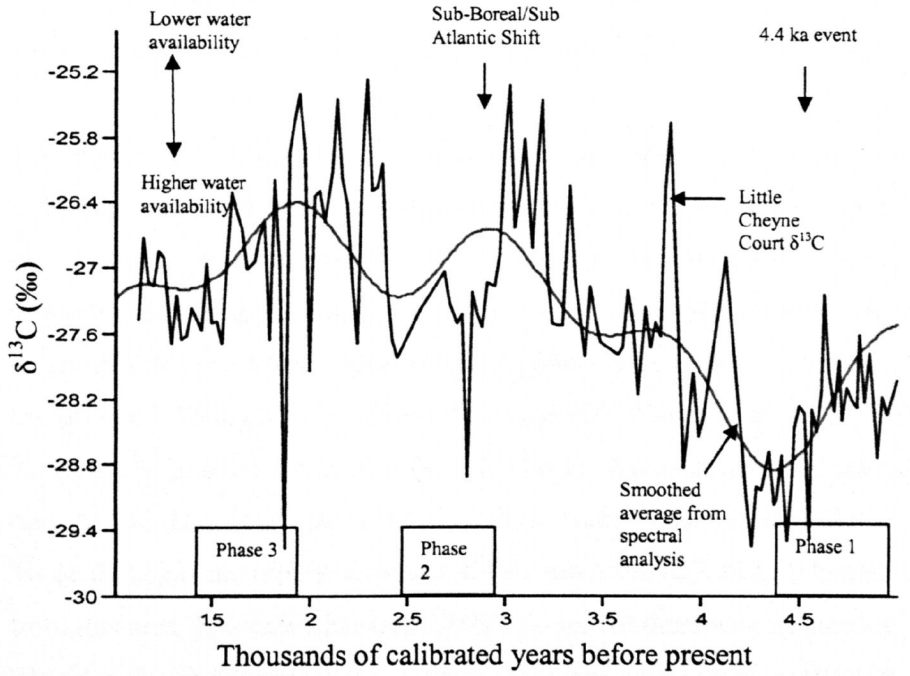


Figure 7.2: *Change in $\delta^{13}C$ for the Little Cheyne Court core (in blue) and identified statistically significant cycles (in red)*

Phase 1 (4800-4400 cal. yrs BP) comprises a consistent shift towards more negative $\delta^{13}C$, from –27.5‰ to –28.8‰ reaching a minimum at around 4450 cal. yrs BP. These conditions of higher water availability led to the establishment of bog vegetation communities. Over the next 400 years there is a large shift towards less negative $\delta^{13}C$ (to around –27.6‰). Climate shifts at this time have been found elsewhere, such as a 1.5°C decline in July air temperature in Norway (Velle *et al.*, 2005). This so-called '4.4ka event' is also identified by Chang and Patterson (2005) at Effingham Inlet, British Columbia, and is associated with generally cooler temperatures. Perry and Hsu (2000) have linked the 4.4ka event to solar-output which steadily decreased up to 4000 cal. yrs BP. This large shift, identified in the isotope record from Little Cheyne Court, was not identified in the pollen record by Waller *et al.* (1999). A phase of lower water availability follows and continues until 3320 cal. yrs BP, with a maximum $\delta^{13}C$ of –26.2‰. This may have promoted the switch to Cyperaceae- and Poaceae-dominated communities seen in zone 6 (see Chapter 6.2.1). During phase 2 there is a second shift towards higher water availability during the Cyperaceae and Poaceae domination which coincides with the Sub-Boreal/Sub-Atlantic transition (Kilian *et al.*, 1995; van Geel *et al.*, 1996), and appears to have persisted until around 2400 cal. yrs BP. The final phase (3), from 1900 to 1400 cal. yrs BP, saw the return of ombrotrophic bog species. The $\delta^{13}C$ values generally decrease from around –26.4‰ to –27.6‰ over this period.

The above discussion suggests that water availability may have had a strong influence over the vegetation communities found at Little Cheyne Court. The cause of the change in water availability is less clear. The availability of water for the vegetation is influenced mainly by relative sea level (RSL) change (and thus the height of the water table) and also precipitation. Little Cheyne Court was one of the last areas of Walland Marsh to become inundated (Waller *et al.*, 1999) and therefore is relatively isolated from the effects of sea level change. For the period from the mid- to late- Holocene there are few sea level index points (see Waller *et al.*, 1999). Those that exist are of low accuracy which makes the RSL history harder to decipher from this area. It is clear that from 7000 cal. yrs BP there was an increase in the rate RSL rise, which slowed from *c.* 6000 to 4000 cal. yrs BP. It was this reduction in the rate of sea level rise, from 2-4mm/year to less than 1mm/year which allowed the

establishment of the barrier, and thus protection for the back-barrier sites. A more detailed discussion of the establishment of the barrier and its eventual breakdown is given in Section 3.2. This correlates well with the $\delta^{13}C$ record which indicates that there was a higher water availability until *c.* 4400 cal. yrs BP. Waller *et al.* 1999 identified a period of reduced RSL rate from *c.* 4000 to *c.* 3400 cal. yrs BP which would lead to a reduction in the height of the water table. Figure 7.2 shows that during this period the $\delta^{13}C$ became less negative, which would indicate lower water availability. From *c.* 3400 cal. yrs BP it is thought that the rate of RSL rise increased once again in the Romney Marsh area (Waller *et al.*, 1999). However the data from this study indicates that while the $\delta^{13}C$ plateaus during the period *c.* 3600 to *c.* 3400 cal. yrs BP, from 3400 cal. yrs BP it appears that there becomes less water available, which is the opposite of what would be expected. This is the period during which acidophilic bog formed, and precedes the replacement of the bog by a Cyperaceae-dominated vegetation community. It is possible to hypothesise that this period represents a time of lower precipitation levels in the local coastal area. This would facilitate the establishment of Cyperaceae-dominated communities in the area. From around 3000 to 200 cal. yrs BP the RSL history is less clear. While not being able to consider the effects of the height of the water table during this time it would appear that the Sub-Boreal/Sub-Atlantic boundary has affected the $\delta^{13}C$ record. During this period the $\delta^{13}C$ became more negative until *c.* 2500 cal. yrs BP, which coincides with a shift towards warmer and wetter conditions in the region (e.g., Hughes *et al.*, 2000; Langdon *et al.*, 2005). From *c.* 2000 cal. yrs the RSL rose by probably 1 - 1.5 m, which would raise the height of the water table and increase water availability. This appears to be the case in the Little Cheyne Court record as $\delta^{13}C$ becomes more negative. The core has not been sampled to the point when marine inundation occurred.

The majority of the samples have $\delta^{13}C$ which are within 1‰ of the smoothed average (see Figure 7.2). There is still, however, a number of larger fluctuations which deviate significantly from the smoothed average. Since the C/N of these samples are typical of the surrounding samples it is unlikely that there is a temporary change in plant material type being investigated. These fluctuations could simply be explained through inter-sample variability (see Figure 6.5). However, the fluctuation

from −28.8 to −25.7‰ and back to −27.6‰ at 3850 cal. yrs BP occurs over five sample points, and represents around 100 years of sedimentation. The fluctuation is therefore unlikely to be due to inter-sample variability. It is more likely therefore that local factors are influencing the record. The fluctuation at 3850 cal. yrs BP may be the result of a temporary shortage of water, for example by lower levels of precipitation or a lowering of the water table, or samples were from a hummock and so were higher than the water table. Fluctuations of similar magnitude found at 3200-2900 cal. yrs BP are more likely to reflect climatic instability. This occurs just before the Sub-Boreal/Sub-Atlantic boundary (van Geel *et al.*, 1996) and so may be related to regional climatic instability, such as increased storminess. A similar degree of variability exists from around 2500-1700 cal. yrs BP. Studies from mid to late Holocene raised bogs elsewhere show that this period was characterised by increased wetness (Aaby, 1976; Ellis and Tallis, 2000; Hughes *et al.*, 2000; Barber *et al.*, 2003; Barber *et al.*, 2004).

From the above discussion it appears that the rate of relative sea-level rise and changes in the amount of precipitation are one of the greatest controls on changing the isotope values. Trends have been identified which transcend vegetation communites and thus indicate a longer term driving process. Since these trends correspond to regional changes in precipitation and also to changes in local RSL it is hard to determine which is the dominant driver for the isotope record, and in reality it is likely that both are working in conjunction. There needs to be much more research of mid- to late- Holocene peat deposits in south-east England before a robust conclusion of the influence of local coastal conditions on the $\delta^{13}C$ can be made.

7.3.2 Hope Farm

The age model for Hope Farm also assumes a constant rate of sedimentation between radiocarbon dated peat samples, based on Waller *et al.* (1999). However the age model at Hope Farm is problematic because sedimentation rates appear rather variable through the profile. The sedimentation rate varies between 0.18 and 2.50 mm/year (1cm represents 4 – 57 years of deposition) assuming a constant rate of sedimentation. Therefore the application of spectral analysis may have limited success in the revealing cycles in the record. Alder-dominated environments are

sensitive to changes in table, since the water they rely on waterlogged conditions to sustain the community (McVean, 1953). Therefore it is reasonable to hypothesise that the development of the alder-dominated carr may record changes in precipitation, in much the same way as the ombrotrophic bog at Little Cheyne Court.

Cycles within the Hope Farm $\delta^{13}C$ record

Spectral analysis has been used to determine whether there are any statistically significant cycles found in the Hope Farm core. The period of deposition of herbaceous fen, alder-dominated carr, Cyperaceae-dominated, *Salix*-dominated and *Myrica*-dominated communities has been sampled. Therefore this does not include the early saltmarsh pre- *c.* 5300 cal. yrs BP, or the most recent herbaceous fen (post *c.* 2000 cal. yrs BP) since these are likely to have been influenced by other coastal processes such as marine inundation (and thus preservation of allochothonous marine material).

Figure 7.3 shows that no statistically significant cycles exist in the Hope Farm core. Furthermore, the shifts towards wetter conditions seen in the Little Cheyne Court (4600-4400, 2800-2400 and 1900-1400 cal. yrs BP) are not apparent in the $\delta^{13}C$ or C/N from the alder carr communities at Hope Farm. This will most likely be due to the age model described, as it is unlikely that the sedimentation rate was as variable as suggested. It is not possible, therefore, to easily correlate changes in precipitation or the height of the water table (and thus RSL) to the Little Cheyne Court core, despite them likely to significantly affect the development of the alder-dominated carr. The change in dominant species composition from *Alnus* (4500-3200 cal. yrs BP) to *Salix* (2950-2320) is the main driver for changes in the $\delta^{13}C$ (Figure 7.4). *Salix* prefers less eutrophic conditions (Dupont *et al.*, 1987) and so it may imply that between 4200 and 3500 cal. yrs BP there was a general trend towards nutrient poor and less acidic conditions. This coincides with a period of gradual drying out in the Little Cheyne Court according to the $\delta^{13}C$.

Influences on the $\delta^{13}C$ at Hope Farm

Waller *et al.* 1999 described how the rise in RSL during peat formation of the alder-dominated carr led to waterlogging conditions, which are necessary for regeneration

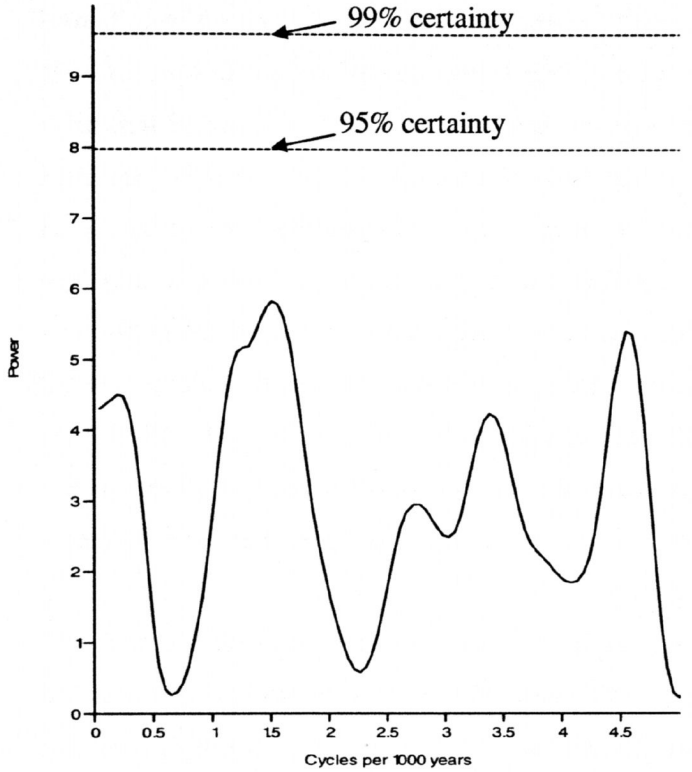


Figure 7.3: *Spectral analysis from Hope Farm (excluding saltmarsh). The two dotted lines indicate 95% and 99% statistical significance*

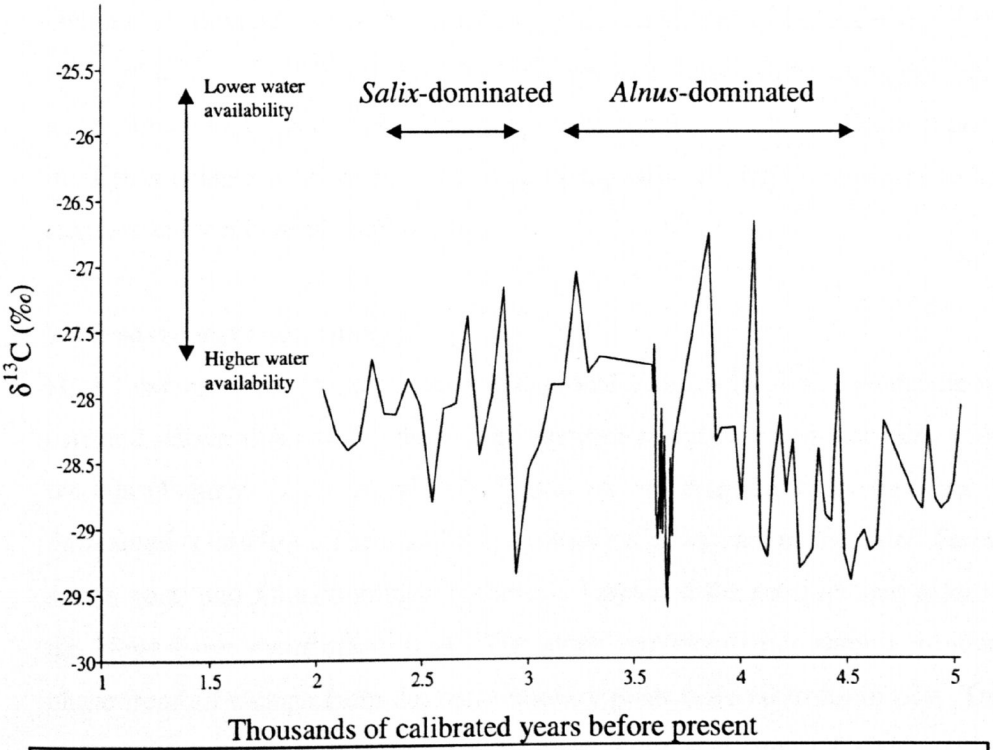


Figure 7.4: *Change in $\delta^{13}C$ for Hope Farm alder-dominated carr deposition*

of the woodland (McVean, 1953). The period from *c.* 6000 to *c.* 4000 cal. yrs BP has been identified as a period of gradual reduction in the rate of RSL rise (leading to the formation of the barrier) and the establishment of peat-forming communities. From *c.* 4000 to *c.* 3400 cal. yrs BP the rate of RSL rise reduced once again which may be witnessed in the $\delta^{13}C$ record as the trend towards less negative values between *c.* 4100 and 3700 cal. yrs BP. Between *c.* 3700 and *c.* 3600 cal. yrs BP in the Hope Farm record the sedimentation rate appears to increase dramatically (each cm representing around 3 years of sedimentation). The $\delta^{13}C$ record at this time indicates a period of higher water availability (with more negative values) and so this part of the core could perhaps correlate with the renewed period of RSL rise from *c.* 3400 cal. yrs BP. If there was a period of reduced precipitation at this time (as possibly seen in the Little Cheyne Court core) then it is not the dominant control on $\delta^{13}C$ and alder carr development at Hope Farm.

The contemporary study of alder carr environments have shown that $\delta^{13}C$ variability between soil samples exists, with variations of up to 1.6‰, despite samples being collected from the same alder carr woodland. For the majority of the $\delta^{13}C$ record, contiguous samples are within 1.6‰ of each other. On three occasions there are shifts of $\delta^{13}C$ (at *c.* 4060, 3850, 2890 cal. yrs BP). Thses shifts also coincides with anomalously high C/N values, generally twice as high as surrounding samples. This implies a change in plant material type being sampled, rather than any temporary changes in local coastal conditions.

7.4 Post-depositional changes

Here I examine the impact of post-depositional changes on $\delta^{13}C$ in alder-dominated carr and saltmarsh since they have been sampled in both the contemporary and fossil records (Figures 7.5, 7.6 and 7.7). I start by splitting the alder carr into *Salix*-dominated (Old House Farm and the most recent alder carr in the Hope Farm main marsh peat) and *Alnus*-dominated (Carter's Farm and the most ancient alder carr in the Hope Farm main marsh peat). The alder carr woodlands show a similar two-phase trend of change from the contemporary plant material to fossil peat. The first phase is an increase in $\delta^{13}C$ (+2.4‰ for *Salix*-dominated carr and +0.6‰ for *Alnus*-dominated carr), from the plant material to the soil material. Early diagenesis of plant

material normally leads to preferential preservation of lignin compared to cellulose and hemi-cellulose components (e.g., Benner, 1984a; b; Benner *et al.*, 1987; 1991). Lignin is depleted in ^{13}C (so has more negative $\delta^{13}C$ value) by around 2-6‰ as investigated in saltmarsh plant materials (Benner *et al.*, 1987; Wilson *et al.*, 2005b), and so it would be expected that decomposing plant material would have more negative $\delta^{13}C$ compared to its original plant vegetation. In woody communities the proportion of carbon by mass derived from lignin is relatively high (Benner *et al.*, 1987) so an even greater negative shift in $\delta^{13}C$ would be expected. The data from this study shows that the opposite pattern occurs. Wilson *et al.* (2005b) predicted the surface sediment $\delta^{13}C$ of a saltmarsh in the Mersey Estuary based on the plant species found, and these were consistently more negative than the observed measurements. Furthermore, taking into account the predicted effects of decomposition (e.g., increased proportion of lignin) the $\delta^{13}C$ of surface sediments were even less negative than expected. In this case it appears that the post-depositional signal has been contaminated by other processes. C4 plants, such as *Spartina townsendii* typically have $\delta^{13}C$ of around −17‰ (Smith and Epstein, 1971; Thomas and Long, 1978; Peterson and Fry, 1987). Furthermore, it is more likely that much of the plant material is being lost from the ecosystem (supported by the low percentage of carbon in the sediment), and secondly marine algae is being brought in with tides, which have less negative $\delta^{13}C$ values (e.g., Mackie *et al.*, 2005). The low C/N (typically below 20) support the notion of tidally derived sediments since aquatic derived vegetation (in particular plankton) tend to have C/N around 4-10 (Meyers, 1994; Meyers and Teranes, 2001).

In the case of the *Alnus* and *Salix*-dominated carr environments the apparent slight positive shift in $\delta^{13}C$ from contemporary plant to contemporary soil material may be the result of other organic carbon present in the sediment, for example from micro-organisms and fungi.

The second phase of change is from the contemporary soil to fossil soil. For the alder carr environments there is a negative shift in $\delta^{13}C$, which is more pronounced in the *Salix*-dominated alder carr. Despite this shift, the final soil $\delta^{13}C$ values are still less negative when compared to the mean plant material $\delta^{13}C$. This once again implies

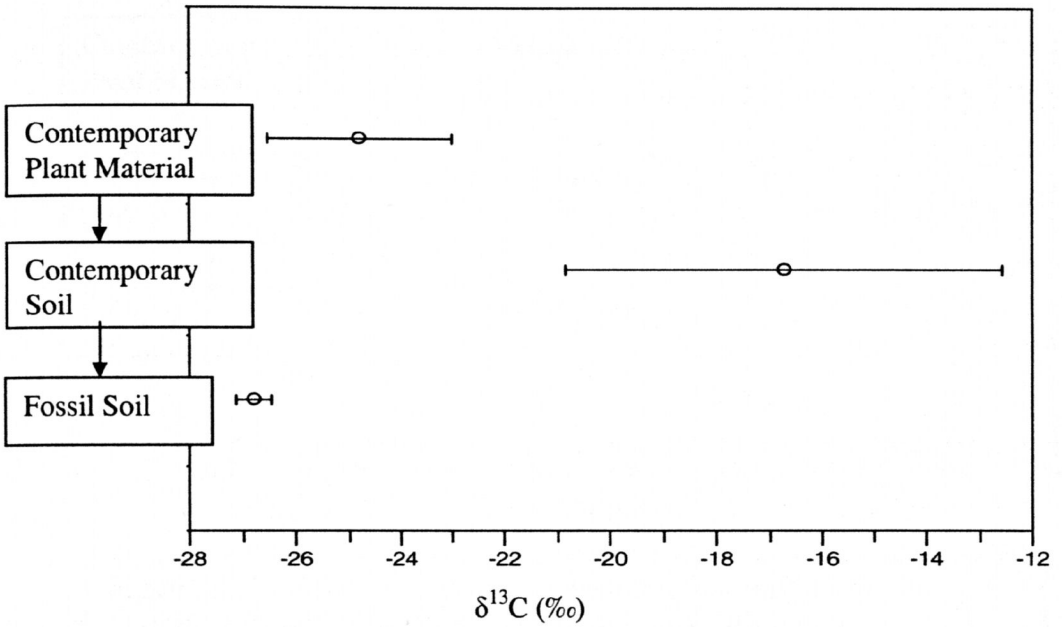


Figure 7.5: *Change in $\delta^{13}C$ from contemporary plant material to contemporary soil to fossil soil of Romney Marsh saltmarsh communities.*

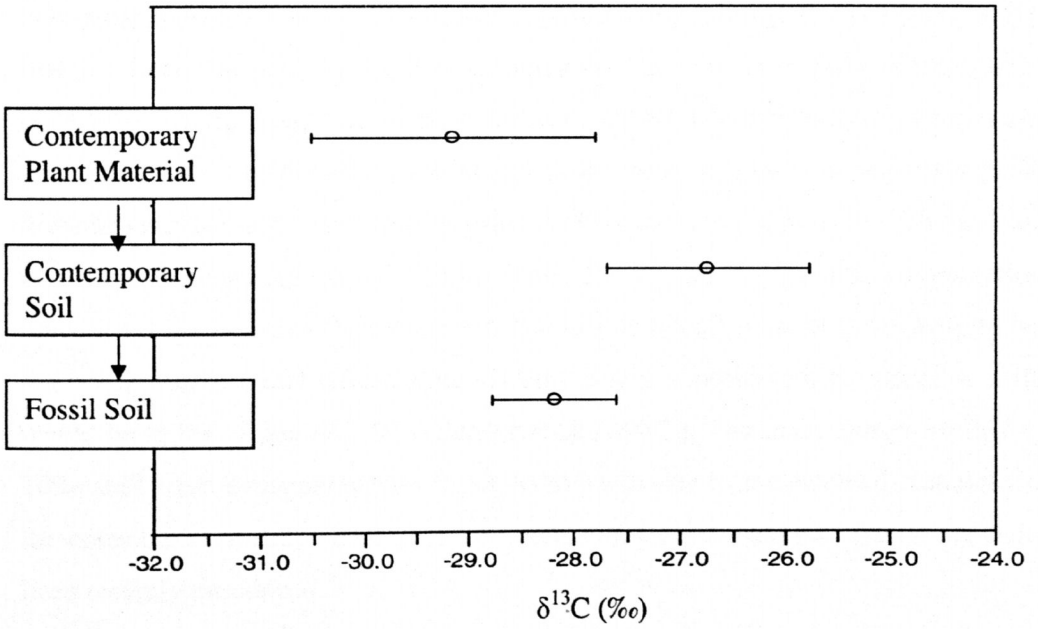


Figure 7.6: *Change in $\delta^{13}C$ from contemporary plant material to contemporary soil to fossil soil of* Salix*-dominated alder carr.*

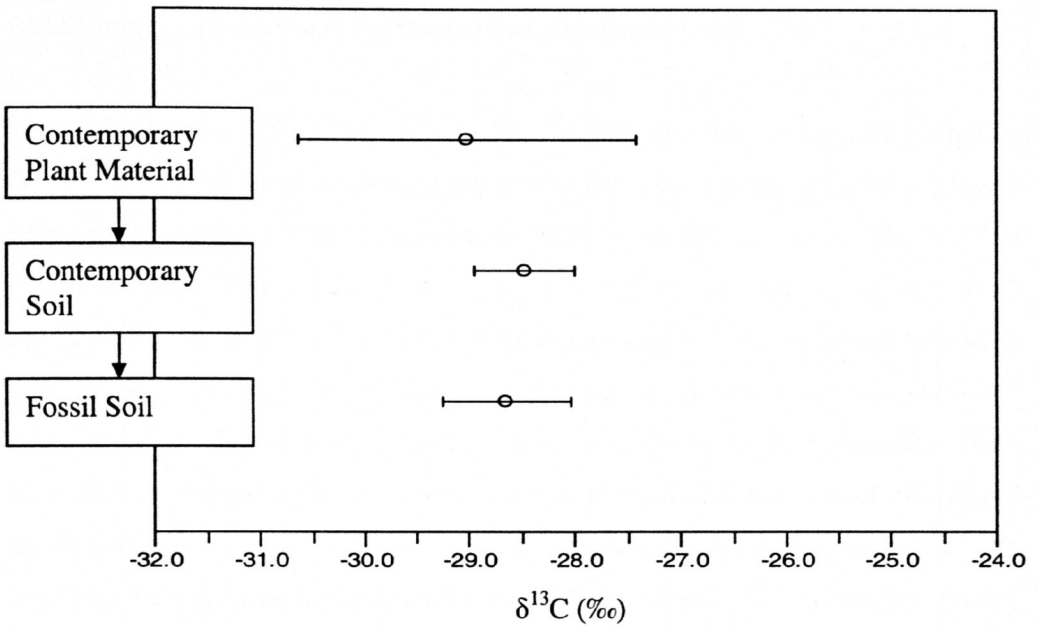


Figure 7.7: *Change in $\delta^{13}C$ from contemporary plant material to contemporary soil to fossil soil of* Alnus*-dominated alder carr*

that the effects of decomposition on the $\delta^{13}C$ are limited, and that the final soil $\delta^{13}C$ is broadly representative of the original vegetation community. It can also be noted that the final soil $\delta^{13}C$ of the *Salix*-dominated alder carr is slightly less negative (–28.2‰) than the *Alnus*-dominated alder carr (–28.6‰). While these differences are still within the error bounds of variability of the peat samples it appears that *Salix* domination generally leads to less negative $\delta^{13}C$ in the fossil core record. The shift in $\delta^{13}C$ from the contemporary soil to fossil soil for saltmarsh vegetation communities reveals a large negative shift from –16.7‰ to –26.8‰. This shift is unlikely to be due to decompositional effects alone (if only lignin is preserved, the negative shift would be in the region of 2-6‰ (Benner *et al.*, 1987)). The main reason for this *c.* 10‰ shift from contemporary to fossil sediment is due to the sampled material. In the cores the saltmarsh would have not sampled C4 plant material, since it has only been recently introduced.

Directly comparing the contemporary plant material to the final soil $\delta^{13}C$ of their respective vegetation communities indicates that the amount of variability between samples is reduced in the fossil soil. A consequence of this is that despite species

variations in the contemporary environments, the final soil carbon isotopic signature will be broadly representative of the original vegetation community.

The plant material C/N, as has already been discussed, tends to vary depending on the type of plant material being sampled, with a trend for increasing C/N from leaf to stem to root and twig material, as the proportion of nitrogen decreases. The soil C/N represents the decomposed plant material and thus an average of the plant components. These values therefore represent changes in the proportion of plant material type, especially in the fossil context. In the carr environments, there is a slight difference between the *Salix* and *Alnus* dominated communities. The *Salix*-dominated contemporary alder carr have lower C/N of 12.7 ± 1.1, while the *Alnus*-dominated alder carr have C/N of 15.6 ± 2.6. These C/N ratios are much lower than would be expected, and are likely to be due to the avoidance of large woody material when sampling. In the fossil environments (excluding those containing one large plant macrofossil), the differences between the *Salix* and *Alnus* dominated alder carr become less apparent. The *Salix*-dominated alder carr have C/N values of 28.8 ± 5.2, while the *Alnus*-dominated alder carr have C/N values of 25.2 ± 5.4. Although the difference between the two environments is clearly within the margins of error, they may be related to the preferential decomposition of woody material in the *Salix*-dominated alder carr. *Salix* tend to occupy wetter and less eutrophic soils than *Alnus* (Dupont, 1987), which would theoretically mean that less aerobic decomposition would occur, perhaps preserving woody material.

C/N for the alder carr vegetation communities are both considerably higher than that of the saltmarsh environments found at Hope Farm and Little Cheyne Court. The average saltmarsh C/N for both sites was 19.1 ± 4.6, however the Little Cheyne Court saltmarsh samples did appear to have slightly higher values (20-24) compared to Hope Farm (12-15). The percentages of carbon and nitrogen preserved in the saltmarsh sediment are low, thus small changes in the amount of carbon or nitrogen can lead to larger changes in the C/N.

Lamb *et al.* (2007) note that there could be alteration of the $\delta^{13}C$ signature as a result of core storage. In their study, using cores from the Humber Estuary, a 0.9‰

increase in $\delta^{13}C$ was observed over a nine year period. Their cores were stored at around 18°C (Lamb *et al.*, 2007), and so fungal growth may have preferentially decomposed lignin (Vane *et al.*, 2003). Although to prevent fungal growth completely would require cores to be stored at or below –5°C (Held *et al.*, 2005) the storage of around 4°C (as in the case of the Hope Farm and Little Cheyne Court cores) is likely to have meant that the $\delta^{13}C$ alteration will be negligible.

7.5 Conclusions

This chapter has examined the $\delta^{13}C$ and C/N of the Hope Farm and Little Cheyne Court cores to investigate their use as a palaeoenvironmental tool. For the mid to late Holocene period it is shown that changes in atmospheric carbon are insufficient to influence the carbon isotopic signatures of vegetation communities. $\delta^{13}C$ and C/N data suggests that there have been influences on the vegetation communities from the local coastal conditions. This has included changes in relative sea level (and thus the height of the water table) and also changes in precipitation. Post-depositional changes are also observed for two important vegetation communities (saltmarsh and alder-dominated carr). Although there are limitations to the use of $\delta^{13}C$ and C/N, as described, nevertheless this work demonstrates the great potential for using the geochemical analyses as a new and complementary tool for understanding the palaeoenvironments.

Chapter 8: Conclusions

8.1 Introduction

This chapter concludes the thesis by reviewing the original aims and objectives and summarising the main project findings. It considers the limitations of the research and finishes by considering suggested directions for future research.

8.2 Main project findings

The main aim of this research was to explore the potential of stable carbon isotope geochemistry to reconstruct past coastal wetlands (see Chapter 1.2). The chosen coastal wetland was Romney Marsh, selected due to the large volume of palaeoenvironmental studies which have been carried out in it over the last few decades (Eddison and Green, 1988; Eddison, 1995; Eddison *et al.*, 1998; Long *et al.*, 2002). To achieve this aim, five objectives provided a basis for the research:

Objective 1 – to review published and newly collected data regarding the carbon isotope and C/N ratios of contemporary vegetation communities and their soils.
A total of 93 plant (leaf, stem, twig and root) and 25 soil samples were sampled from four alder-dominated carr woodlands and one saltmarsh in Romney Marsh and the Norfolk Broads. These environments were selected because they represent important mid Holocene vegentation communities in the Romney Marsh area.

Plant material from saltmarsh has much less negative $\delta^{13}C$ than alder carr material (–22.5‰ to –26.5‰ compared to –26‰ to –32‰). Leaf material have lower C/N (around 20) than woody material (typically over 40), and thus plant material type can be differentiated. Soil $\delta^{13}C$ for both the alder carr and saltmarsh communities tend to be less negative relative to the plant material found within their vegetation community (+0.5‰ for alder-dominated carr and +8‰ for saltmarsh) The C/N of soils are around 20, most closely relating to the leaf material. These results are comparable to previous studies.

Certain species are more important in influencing the final soil isotopic and C/N ratio. In alder carr communities, for example, *Salix* spp. has less negative (on

average) $\delta^{13}C$ than *Alnus glutinosa* by 1.2‰ for leaf material and 1.8‰ for woody material (see Chapter 5.2.3). The species composition of a particular vegetation community has been shown to influence the isotope ratio of their soils (see Figure 5.5). In the contemporary environment the effects of temperature, precipitation and geological changes may each also potentially influence the isotopic ratios of the plant material.

Objective 2 – to review published and newly collected data regarding the carbon isotope and C/N ratios of fossil vegetation communities and their soils.

Two sites from Romney Marsh, Hope Farm and Little Cheyne Court (see Chapter 3.3) contain sediments that formed under seven different vegetation communities and over a period of *c.* 4000 years of peat deposition. A 1 cm contiguous sampling strategy through the two metre thick sequences of peat at each site generated a total of 234 samples which have been tested for their $\delta^{13}C$ and C/N.

Different vegetation communities cannot be differentiated based on a combination of $\delta^{13}C$ and C/N, however some general patterns have emerged. Saltmarsh sediments have $\delta^{13}C$ of –26.6‰ to –27.1‰ and C/N of 18 to 28. Cyperaceae-dominated vegetation and ombrotrophic bog sediments have $\delta^{13}C$ generally of –25.5‰ to –28.5‰, but average C/N of Cyperaceae-dominated vegetation is 53 and ombrotrophic bog is 40. Alder-dominated carr has $\delta^{13}C$ of –27.4‰ to –29.6‰ while the C/N is generally between 20 and 40. The remaining sampled communities (*Myrica gale*-dominated, fen and poor fen), due to overlapping ranges in their geochemical data, are in no way distinguishable from each other based on their geochemical signatures..

Comparison to other UK and northern Europe sites shows a positive gradient in $\delta^{13}C$ from alder-dominated carr fen, Cyperaceae-dominated, ombrotrophic bog to saltmarsh (see Chapter 6.5). Alder-dominated carr has typical $\delta^{13}C$ of –28.5 ± 1.5‰, fen has $\delta^{13}C$ of –28.3 ± 2.2‰, Cyperaceae-dominated vegetation has $\delta^{13}C$ of –28.4 ± 1.7‰, ombrotrophic bog has $\delta^{13}C$ of –27.2 ± 2.6‰ and saltmarsh has $\delta^{13}C$ of –26.2 ± 3.0‰. This compares well to the data from this study of alder-dominated carr

(−28.7 ± 2.6‰), fen (−27.7 ± 1.0‰), Cyperaceae-dominated vegetation (−27.0 ± 1.7‰), ombrotrophic bog (−27.1 ± 1.7‰), and saltmarsh (−26.8 ± 0.7‰).

Objective 3 – to compare the carbon isotope and C/N ratios of contemporary and fossil vegetation communities.

Sampled soil material shows a decrease in $\delta^{13}C$ from contemporary to fossil environments (−0.2‰ for alder-dominated carr and −10‰ for the saltmarsh environment). There is also evidence to suggest that species which were influencing the contemporary soil isotopic ratios are also influencing the fossil core record, particularly with changes from C3 to C4 dominated environments. The Hope Farm record contains two phases of alder carr woodland, one of which was dominated by *Salix*, and the other by *Alnus*. The *Salix* spp. dominated alder carr has $\delta^{13}C$ ratios which are around 0.4‰ less negative than the *Alnus* dominated alder carr.

Objective 4 – to investigate the effects of local coastal conditions, geology, and source atmospheric carbon on the carbon isotope and C/N ratios.

Changes in local coastal conditions have been shown to have a great effect on the $\delta^{13}C$ ratios in Romney Marsh, especially Little Cheyne (predominantly fen communities and ombrotrophic bog). Spectral analysis reveals two cycles of 1005 and 1675 year cycles exist in the record (see Chapter 7.3.1) that are comparable to other raised bog sequences (e.g., Langdon *et al.*, 2003). Phases where there were shifts towards higher water availability have been identified at 4600-4400, 3200-2700 and 2200-1500 cal. yrs BP, which correlate to similar shifts found in many other raised bogs in north-west Europe (e.g., van Geel *et al.*, 1996; Barber *et al.*, 2003; Langdon *et al.*, 2005). The strongest shift occurs from 4500-4000 cal. yrs BP and is contemporaneous with the '4.4 ka BP event'. The decrease in $\delta^{13}C$ in the Little Cheyne Court record at this time implies a period of cooling which coincides with a significant decrease of solar activity at 4400 cal yrs BP (Perry and Hsu, 2000). It has also been shown that changes in relative sea level have had a major influence on the water availability (see Chapter 7.3.1) and are considered to be one of the main drivers of changes in vegetation and also the $\delta^{13}C$ of the sediments sampled.

It has also been shown that source atmospheric carbon is a major influence on the final $\delta^{13}C$ of the sediment and plant material. Since 1850 the $\delta^{13}C$ of atmospheric carbon has decreased by around 1.7‰ (McCarroll and Loader, 2004) which complicates comparison between contemporary vegetation material, recently deposited sediment and Holocene sediments. During the mid- to late- Holocene period the evidence indicates that changes in atmospheric carbon $\delta^{13}C$ were small (in the order of 0.1 – 0.2‰ (Indemühle, *et al.*, 1999)).

Objective 5 – to provide a greater understanding of wetland dynamics in the Romney Marsh region.

Changes in vegetation communities clearly influenced the $\delta^{13}C$ and C/N ratios of the fossil peat. Using this information it is possible to identify the effects of changes in local coastal conditions and environmental stress within these communities. One of the most noteable impacts occurs at the top of the Hope Farm core. The uppermost deposited material has been described as a fen community (Waller *et al.*, 1999) although the $\delta^{13}C$ of the fossil sediment significantly increases and C/N falls at this level. These changes are comparable with saltmarsh $\delta^{13}C$ and C/N. Waller *et al.*, (1999) identified polyhabous diatoms in this zone, which implied marine inundation, and is supported by the carbon isotope record. Carbon isotopes and C/N ratios can therefore be used in situations where the exact nature of a vegetation community is disputed.

8.3 Limitations of this project

The limitations of this project relate to potential problems that influence the carbon isotopic and C/N ratios of plants and their soils, assumptions made when interpreting the results, and also the sampling strategies used to collect plant and soil material.

8.3.1 Limitations of using $\delta^{13}C$ and C/N ratios in palaeoenvironmental investigations

Using carbon isotope geochemistry in palaeoenvironmental reconstructions is a new and expanding field, and as yet, is still relatively poorly understood. The impact of precipitation, temperature, salinity, geology and other local processes on the uptake of isotopes of carbon have not been fully researched. Therefore reliance has been put

on theoretical concepts, laboratory experiments and relatively few environmental studies. The inter-relatedness of many of these variables makes it difficult to distinguish unambiguously between the different processes which potentially are causing shifts in $\delta^{13}C$ ratios in vegetation communities.

Post-depositional changes are a potential complication when reconstructing past palaeoenvironments. Diagenetic alteration of both $\delta^{13}C$ and C/N ratios is highly variable and can complicate palaeoenvironmental reconstructions. The selective decay of organic material is not the only consideration to be made when examining post-depositional changes; bacterial action also uses carbon (^{12}C in preference to ^{13}C) and increases the nitrogen content of the soil (Kaplan and Rittenburg, 1964; Benner *et al.*, 1987).

Taken together these processes make it harder to infer past coastal conditions or vegetation communities using geochemical data alone. This problem has been reduced somewhat by relating the isotope record to the palynological record from Romney Marsh.

8.3.2 Limitations in the sampling strategies

Chapter 4.3 has highlighted the main sampling errors and limitations of this study. For the contemporary record the main limitation is the extent to which the field sampling adequately captures the natural variability in the environments under study. It is known that there can be variance in $\delta^{13}C$ within the same plant material type, even if from the same plant (e.g., Kohorn *et al.*, 1994; Twiddy, 1996). To help counter this, as far as possible, an 'average' of the vegetation was collected from each site. In reality, though, this is not possible: leaf, stem and twig material was primarily sampled from up to 2 metres above ground level, meaning that the lower and upper canopies remain unrepresented, despite representing a large proportion of the biomass of the vegetation community. Furthermore, root material was sampled from close to the surface, and may have different isotope and C/N of deeper root material. While it is not thought that the sampling strategy will have significantly affected the isotope and C/N of the plant and soil material, it must remain a consideration. The effect of non-plant organic matter must also be taken into account

in both the contemporary and palaeoenvironmental records. It is difficult to quantify the effects of components such as fungi, microfauna and bacteria, especially in diverse habitats such as alder-dominated carr woodlands and saltmarshes.

Laboratory techniques (see Chapter 4.5) were designed to reduce the amount of material being sampled, while still representing the whole vegetation community. Plant material was reduced in size gradually and selected at random so that the widest range of material was used. The main problem for the palaeoenvironmental record was that, since cored material was being analysed, only 1 cm^3 was used to represent the vegetation community for a particular period of time.

8.4 Future research

The field of carbon isotope geochemistry and C/N for use in palaeoenvironmental studies is a relatively new one. The research presented in this thesis shows that they can be used alongside other palaeoenvironmental techniques (in this case palynology) to accurately quantify changes in the environment and to test hypotheses regarding driving mechanisms, such as changes in local coastal conditions and relative sea level changes.

Future research should further test the impacts of precipitation and temperature on the investigated vegetation communities, principally alder carr and saltmarsh. Similar studies should be carried out elsewhere around the UK and north-west Europe to compare to this study. Other plant investigated communities found in the cores such as bog, Cyperaceae-dominated vegetation, and poor fen should also be explored in a similar way to assess how the contemporary and fossil environments are related. In terms of Romney Marsh, the $\delta^{13}C$ and C/N of paleao-vegetation communities can easily explored using other cores found in the main marsh peat layer. It would be particularly interesting to learn whether the processes thought to be operating at Hope Farm and Little Cheyne Court are also operating elsewhere in the marsh. Particular emphasis needs to be drawn to providing a study of the contemporary $\delta^{13}C$ and C/N of bog environments to fully understand how bog species react to changes in the height of the water table and changes in precipitation. This would help in

providing more robust conclusions in conjunction with the Little Cheyne Court core record.

Lastly the study has shown that different vegetation communities respond differently to the same forcing factor. Ombrotrophic systems, such as those sampled in Little Cheyne Court appear to respond more directly to climate (especially in relation to precitation change) compared to the less sensitive alder-dominated carr which dominated at Hope Farm. It may be possible to apply the approach here to other previously studied ombrotrophic settings in other coastal and inland depositional environments.

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Appendix A

Plant species abundance of sampled vegetation from contemporary alder carr and saltmarsh communities.

Site number	Canopy	%	Undercanopy	%	Field	Ground
CAL001 N 52 46.527' E 001 34.332'	*Alnus glutinosa*	30	*Alnus glutinosa*	45	*Dryopteris dilatata*	*Rubus fruticosus*
	Betula pubescens	15	*Betula pubescens*	10	*Phragmites australis*	*Sphagnum spp.*
	Quercus robur	10	*Salix cinerea*	25	*Lonicera periclymenum*	*Dryopteris dilatata*
	Sorbus aucuparia	40	*Ilex aquifolium*	5	*Alnus glutinosa*	*Lonicera periclymenum*
	Absent	5	*Quercus robur*	5	*Rubus fruticosus*	*Stellaria media*
			Crataegus monogyna	5	*Iris pseudacorus*	*Thelypteris palustris*
			Frangula alnus	5	*Thelypteris palustris*	*Alnus glutinosa (shoots)*
					Rosa canina	*Salix cinerea (shoots)*
					Quercus robur	*Poaceae undiff.*
CAL003 N 52 46.528' E 001 34.586	*Betula pubescens*	75	*Ilex aquifolium*	20	*Dryopteris dilatata*	*Juncus effusus*
	Quercus robur	10	*Frangula alnus*	10	*Rubus fruticosus*	*Sphagnum spp.*
	Alnus glutinosa	5	*Betula pubescens*	40	*Phragmites australis*	*Poaceae undiff.*
	Sorbus aucuparia	5	*Quercus robur*	20	*Frangula alnus*	
	Betula pendula	5	*Salix cinerea*	5		
			Alnus glutinosa	5		
CAL005 N 52 46.500' E 001 34.304'	*Betula pubescens*	30	*Betula pubescens*	40	*Dryopteris dilatata*	*Juncus effusus*
	Betula pendula	5	*Alnus glutinosa*	45	*Rubus fruticosus*	*Sphagnum spp.*
	Alnus glutinosa	65	*Sorbus acuparia*	10	*Loricera periclymenum*	*Poaceae undiff.*
			Larix decidua	5	*Thelypteris palustris*	
					Juncus effusus	

Table A1: Calthorpe main plant species found, and their abundance in upper and lower canopies.

Site number	Canopy	%	Undercanopy	%	Field	Ground
WH001 N 52 35.863 E 001 26.128	*Quercus robur*	5	*Alnus glutinosa*	5	*Ribes rubrum*	*Hedera helix*
	Alnus glutinosa	10	*Acer pseudoplatanus*	5	*Rubus fruticosus*	*Sphagnum spp.*
	Acer pseudoplatanus	30	*Corylus avellana*	40	*Dryopeteris felix-mas*	*Ligustrum vulgare*
	Fraxinus exelsior	35	*Crataegus monogyna*	5	*Ligustrum vulgare*	*Ribes rubrum*
	Corylus avellana	15	*Fraxinus exelsior*	20	*Hedera helix*	
	Absent	5	Absent	25	*Crataegus monogyna*	
					Solanum dulcamara	
WH002 N 52 35.854 E 001 26.148	*Acer pseudoplatanus*	20	*Acer pseudoplatanus*	25	*Ribes rubrum*	*Phyllitis scolopendrium*
	Alnus glutinosa	40	*Fraxinus exelsior*	5	*Ribes nigrum*	*Hedera helix*
	Fraxinus exelsior	40	*Crataegus monogyna*	15	*Ribes uva-crispa*	*Ligustrum vulgare*
			Corylus avellana	30	*Thelypteris palustris*	*Sphagnum spp*
			Ligustrum vulgare	10	*Urtica dioica*	*Geranium robertianum*
			Alnus glutinosa	15	*Hedera helix*	*Geum urbanum*
					Impatiens capensis	*Chrysosplenium oppositifolium*
					Rubus fruticosus	
					Ligustrum vulgare	*Ranunculus repens*
					Alnus glutinosa	*Viola riviniana*
					Filipendula ulmaria	
WH005 N 52 35.855 E 001 26.221			*Salix cinerea*		*Urtica dioica*	
			Alnus glutinosa		*Iris pseudacorus*	
			Corylus avellana		*Convolvulus arvensis*	
					Rumex sanguineus	
					Eupatorium cannabinum	

					Eupatorium	*Cirsium*
WH006	*Quercus robur*	5	*Quercus robur*	5	*cannabinum*	*palustre*
N 52	*Acer*				*Impatiens*	
35.987	*pseudoplatanus*	5	*Alnus glutinosa*	35	*capensis*	*Hedera helix*
E 001	*Fraxinus*		*Acer*			
26.177	*excelsior*	60	*pseudoplatanus*	5	*Hedera helix*	*Sphagnum spp.*
			Crataegus			*Lapsana*
	Absent	30	*monogyna*	5	*Urtica dioica*	*communis*
			Corylus		*Rubus*	
			avellana	20	*fruticosus*	*Poaceae undiff.*
			Fraxinus		*Phragmites*	
			avellana	15	*Australis*	
					Iris	
			Salix cinerea	5	*pseudacorus*	
					Lapsana	
			Malus sylvestris	5	*communis*	
			Viburnum		*Rumex*	
			opulus	+	*alpinus*	
			Ligustrum		*Thelypteris*	
			vulgare	+	*palustris*	
					Ilex aquifolium	

Table A2: Wheatfen main plant species found, and their abundance in upper and lower canopies.

Site	Canopy	%	Undercanopy	%	Field	Ground
	Fraxinus					
OHF001	*exelsior*	20	*Alnus glutinosa*	20	*Urtica dioica*	*Urtica dioica*
N 50			*Acer*		*Heracleum*	
58.909	*Salix fragilis*	80	*pseudoplatanus*	20	*sphondylium*	*Poaceae undiff*
E 000	*Corylus*		*Crataegus*		*Peucedenum*	*Sphagnum*
41.691	*avellana*	+	*monogyna*	20	*palustre*	*spp.*
			Fraxinus		*Lapsana*	*Ranunculus*
			exelsior	30	*communis*	*repens*
			Prunus spinosa	10		
	Fraxinus					*Sphagnum*
OHF003	*exelsior*	25	*Alnus glutinosa*	30	*Urtica dioica*	*spp.*
N 50			*Acer*		*Heracleum*	*Poaceae*
58.899	*Salix fragilis*	75	*pseudoplatanus*	25	*sphondylium*	*undiff.*
E 000			*Fraxinus*			*Ranunculus*
41.675			*exelsior*	20	*Iris pseudacorus*	*repens*
			Absent	25	*Rumex sanguineus*	
			Acer			*Ranunculus*
OHF004	*Salix fragilis*	50	*pseudoplatanus*	40	*Urtica dioica*	*repens*
N 50	*Populus*		*Fraxinus*		*Heracleum*	*Sphagnum*
58.889	*candicans*	20	*exelsior*	30	*sphondylium*	*spp.*
E 000	*Alnus*					
41.659	*glutinosa*	30	*Prunus spinosa*	30	*Rubus fruticosus*	
			Larex decidua	+	*Salix cinerea*	
					Iris pseudacorus	
					Circaea	*Ranunculus*
OHF005	*Salix fragilis*	70	*Alnus glutinosa*	20	*lutetiana*	*repens*
	Alnus		*Acer*			*Sphagnum*
N 50 58.	*glutinosa*	10	*pseudoplatanus*	20	*Urtica dioica*	*spp.*
E 000	*Populus*				*Heracleum*	
41.	*candicans*	20	*Prunus spinosa*	30	*sphondylium*	
			Absent	30	*Rubus fruticosus*	
						Ranunculus
OHF006	*Salix fragilis*	70	*Alnus glutinosa*	10	*Urtica dioica*	*repens*
	Alnus		*Acer*		*Heracleum*	*Sphagnum*
N 50 58.	*glutinosa*	15	*pseudoplatanus*	10	*sphondylium*	*spp.*
E 000	*Populus*				*Rubus*	
41.	*candicans*	15	*Prunus spinosa*	5	*fruticosus*	
			Crataegus			
			monogyna	5	*Iris pseudacorus*	
			Absent	70	*Galium aparine*	

Table A3: Old House Farm main plant species found, and their abundance in upper and lower canopies.

Site	Upper Canopy	%	Under Canopy	%	Field	Ground
CF001 **N 50** **53.879** **E 000** **41.023**	*Alnus glutinosa*	100	*Alnus glutinosa* *Salix cinerea* Absent	15 15 70	*Rubus fruticosus* *Urtica dioica* *Dryopteris dilatata* *Heracleum sphondylium* *Peucedanum palustre* *Iris pseudacorus*	*Lonicera spp.* *Convulvulus arvensis*
CF002 **N 50** **53 878** **E 000** **41.018**	*Alnus glutinosa*	100	*Alnus glutinosa* *Sambucus nigrum* Absent	10 10 80	*Urtica dioica* *Rubus fruticosus* *Iris pseudacorus* *Dryopteris dilatata*	*Convulvulus arvensis* *Sphagnum spp.* *Valeriana dioica*
CF003 **N 50** **53.864** **E 000** **41.018**	*Alnus glutinosa*	100	*Alnus glutinosa* *Sambucus nigrum* Absent	20 + 80	*Urtica dioica* *Dryopteris dilatata* *Carex pendula* *Cirsium palustre* *Lonicera periclymenum* (Absent 70%)	*Lonicera spp.* *Sphagnum spp.* *Poaceae undiff* *Geranium robertianum*
CF004 **N 50** **53.861** **E 000** **41.993**	*Alnus glutinosa* *Salix fragilis*	90 10	*Alnus glutinosa* *Salix cinerea* *Sambucus nigrum* Absent	10 10 20 60	*Urtica dioica* *Dryopteris dilatata* *Rubus fruticosus* *Geranium robertianum* *Carex pendula* *Cirsium palustre*	*Lonicera spp.* *Valeriana dioica* *Ranunculus repens*
CF005 **N 50** **53.853** **E 000** **41.984**	*Alnus glutinosa* *Salix alba* Absent	60 20 20	*Alnus glutinosa* *Sambucus nigrum* *Salix cinerea* Absent	25 15 30 40	*Urtica dioica* *Rubus fruticosus* *Peucedanum palustre* *Dryopteris dilatata* *Hedera helix* *Carex pendula* *Iris pseudacorus* *Mentha aquatica*	*Sphagnum spp.* *Valeriana dioica* *Poaceae undiff*

Table A4: Carter's Farm main plant species found, and their abundance in upper and lower canopies.

Site	Latitude	Longitude	Species	%
RSM001	50 56.748'	000 45.009'	*Spartina townsendii*	40
			Aster tripolium basal leaves	20
			Seriphidium maritimum	25
			Aster tripolium	15
RSM002	50 56.754'	000 45.046'	*Aster tripolium*	5
			Seriphidium maritimum	95
RSM003	50 56.752	000 45.039	*Aster tripolium*	5
			Seriphidium maritimum	95
RSM004	50 56.751	000 45.032	*Aster tripolium*	5
			Aster tripolium basal leaves	15
			Seriphidium maritimum	80
RSM005	50 56.750	000 45.025	*Spartina townsendii*	20
			Seriphidium maritimum	80
RSM006	50 56.748	000 45.009'	*Spartina townsendii*	10
			Seriphidium maritimum	30
			Limonium vulgare	60
RSM007	50 56.744	000 44.997	*Aster tripolium basal leaves*	10
			Suaeda verna	25
			Spartina townsendii	50
			Seriphidium maritimum	60
			Aster tripolium	5
RSM008	50 57.045	000 44.417	*Salicornia ramossisima*	50
			Festuca rubra	5
			Absent	45
RSM009	50 57.042	000 44.413	*Salicornia ramossisima*	50
			Festuca rubra	20
			Absent	30
RSM011	50 57.018	000 44.471	*Salicornia ramossisima*	60
			Festuca rubra	40
RSM012	50	000	*Salicornia fragilis*	25

	57.012	**44.482**			
			Salicornia pusilla		35
			Festuca rubra		40
	50	**000**			
RSM013	**56.926**	**44.481**	*Salicornia fragilis*		40
			Festuca rubra		60
	50	**000**			
RSM014	**56.901**	**44.637**	*Salicornia fragilis*		50
			Festuca rubra		50
			Spergularia marina	+	
	50	**000**			
RSM015	**56.846**	**44.798**	*Festuca rubra*		50
			Salicornia fragilis		50
			Spergularia marina	+	
			Honkenya peploides	+	
	50	**000**			
RSM016	**56.680**	**45.033**	*Seriphidium maritimum*		90
			Suaeda maritima		10
	50	**000**			
RSM017	**56.661**	**45.078**	*Seriphidium maritimum*		70
			Suaeda maritima		30
	50	**000**			
RSM018	**56.635**	**45.093**	*Seriphidium maritimum*		60
			Limonium vulgare		40

Table A5: Rye Saltmarsh main plant species found, and their abundance within each quadrat. Note: Percentage totals may exceed 100% where layering of vegetation has occurred.

Appendix B

Main plant species found in the investigated Wheatfen alder carr woodland

Acer pseudoplatnus
Alnus glutinosa
Berula erecta
Calystegia sepium
Cardamine amara
Cardamine flexuosa
Carex acutiformis
Carex elata
Carex remota
Carex riparia
Eupatorium cannabium
Filipendula ulmaria
Fraxinus excelsior
Galium palustre
Geranium robertianum
Hedera helix
Humulus lupulus
Ilex aquifolium
Impatiens capensis
Iris pseudacorus
Ligustrum vulgare
Lycopus europaeus
Lysimachia nummularia
Lythrum salicaria
Mentha aquatica
Myosotis scorpoides
Phragmites australis
Phyllitis scolopendrium
Poa trivialis
Polypodium vulgare
Rhammus cathartica
Ribes nigrum
Ribes rubrum
Rosa canina agg.
Rumex sanguineus
Salix cinerea
Solanum dolcamara
Tamus communis
Thelypteris palustris
Urtica dioica
Viburnum opulus

Appendix C

Plant species; material type and soil sampled from the contemporary alder carr and saltmarsh environments

Site	CAL002	CAL003	CAL005
Samples collected	*Alnus glutinosa* leaves	*Alnus glutinosa* leaves	*Betula pubescens* roots
	Alnus glutinosa twigs	*Alnus glutinosa* twigs	Soil Sample E
	Dryopteris dilatata leaves	*Betula pubescens* leaves	Soil Sample F
	Dryopteris dilatata stems	*Betula pubescens* twigs	
	Phragmites australis leaves	*Rubus fruticosus* leaves	
	Salix cinerea leaves	*Rubus fruticosus* stems	
	Salix cinerea twigs	Soil Sample C	
	Salix cinerea roots	Soil Sample D	
	Soil Sample A		
	Soil Sample B		

Table C1: Calthorpe plant samples, and soil samples, used for carbon isotope analysis.

Site	WH001	WH002	WH003	WH005	WH006
Samples collected	*Alnus glutinosa* leaves	*Alnus glutinosa* leaves	*Eupatorium cannabinu m* leaves	*Alnus glutinosa twigs*	Soil sample E
	Alnus glutinosa twigs	*Alnus glutinosa* twigs		*Salix cinerea* leaves	Soil sample F
	Alnus glutinosa roots	*Rubus fruticosus* leaves		*Salix cinerea* twigs	
	Rubus fruticosus stems	Soil Sample B		Soil sample D	
	Soil Sample A	Soil Sample C			

Table C2: Wheatfen plant samples, and soil samples, used for carbon isotope analysis.

Site	OHF001	OHF003	OHF004	OHFH005	OHFH006
Samples collected	*Alnus glutinosa* leaves	Soil Sample B	*Alnus glutinosa* leaves	Soil Sample C	*Alnus glutinosa* leaves
	Alnus glutinosa twigs		*Alnus glutinosa* twigs		*Alnus glutinosa* twigs
	Salix fragilis leaves		*Alnus glutinosa* roots		*Salix fragilis* leaves
	Salix fragilis twigs		*Rubus fruticosus* leaves		*Salix fragilis* twigs
	Urtica dioica leaves		*Rubus fruticosus* stems		*Salix fragilis* twigs
	Urtica dioica stems		*Salix fragilis* leaves		Soil Sample D
	Soil Sample A		*Salix fragilis* roots		Soil Sample E
			Urtica dioica leaves		
			Urtica dioica stems		

Table C3: Old House Farm plant samples, and soil samples, used for carbon isotope analysis.

Site	CF001	CF002	CF003	CF004	CF005
Samples collected	*Alnus glutinosa* leaves	Soil Sample B	*Alnus glutinosa* leaves	*Rubus fruticosus* leaves	*Alnus glutinosa* leaves
	Alnus glutinosa twigs		*Alnus glutinosa* twigs	*Rubus fruticosus stems*	*Alnus glutinosa* twigs
	Alnus glutinosa roots		*Alnus glutinosa* twigs	*Salix alba* leaves	*Alnus glutinosa* twigs
	Dryopteris dilatata leaves		*Alnus glutinosa* roots	*Salix alba* twigs	*Rubus fruticosus* stems
	Rubus fruticosus leaves		*Dryopteris dilata* leaves	*Salix cinerea* leaves	Soil sample E
	Rubus fruticosus stems		*Urtica dioica* leaves	*Salix cinerea* twigs	
	Salix cinerea leaves		*Urtica dioica* stems	Soil sample D	
	Salix cinerea twigs		Soil Sample C		
	Salix cinerea roots				
	Urtica dioica leaves				
	Urtica dioica stems				
	Soil Sample A				

Table C4: Carter's Farm plant samples, and soil samples, used for carbon isotope analysis.

Site	**RSM001**	**RSM002**	**RSM004**	**RSM006**	**RSM007**	**RSM008**
Samples collected	*Aster tripolium* leaves	*Aster tripolium* basal leaves	*Seriphidium maritimum* leaves	*Limonium vulgare leaves*	*Suaeda verna* leaves	*Festuca rubra*
	Aster tripolium stems		Soil sample B	*Limonium vulgare stems*		
	Aster tripolium basal leaves			*Festuca rubra*		
	Seriphidium maritimum stems					
	Seriphidium maritimum leaves					
	Festuca rubra					
	Soil sample A					
Site	***RSM009***	***RSM011***	***RSM012***	***RSM014***	***RSM017***	
Samples collected	*Salicornia ramossisima*	*Salicornia ramossisima*	*Festuca rubra*	*Salicornia fragilis*	*Seriphidium maritimum* leaves	
		Soil sample D	*Salicornia fragilis*	Soil sample F		

Table C5: Rye Saltmarsh plant samples, and soil samples, used for carbon isotope analysis.

Appendix D

Contemporary $\delta^{13}C$ and C/N ratios and %C, %N for contemporary alder carr and saltmarsh environments

Site No:	Species	Material type	$\delta^{13}C$ (‰)	C/N	%C	%N
CAL002	*Alnus glutinosa*	Leaf	-32.0	11.0	44.0	4.0
CAL002	*Dryopteris dilatata*	Leaf	-30.1	18.8	44.2	2.3
CAL002	*Salix cinerea*	Leaf	-31.5	20.3	46.7	2.3
CAL002	*Salix cinerea*	Root	-28.7	77.4	44.9	0.6
CAL002	*Alnus glutinosa*	Twig	-33.2	53.8	46.9	0.9
CAL002	*Salix cinerea*	Twig	-29.7	79.5	47.2	0.6
CAL002	Soil Sample A		-28.2	15.3	33.2	2.2
CAL002	Soil Sample A		-29.1	15.8	40.7	2.6
CAL002	*Phragmites australis*	Leaf	-30.7	13.7	42.1	3.1
CAL002	*Dryopteris dilatata*	Stem	-29.7	64.2	42.1	0.7
CAL003	*Alnus glutinosa*	Leaf	-30.5	18.0	20.7	1.2
CAL003	*Betula pubescens*	Leaf	-29.1	20.4	47.8	2.3
CAL003	*Rubus fruticosus*	Leaf	-29.7	18.1	46.4	2.6
CAL003	*Rubus fruticosus*	Stem	-28.8	52.4	44.7	0.9
CAL003	*Alnus glutinosa*	Twig	-30.7	60.0	49.8	0.8
CAL003	Soil Sample C		-28.3	17.8	38.8	2.2
CAL003	Soil Sample D		-28.4	17.7	44.5	2.5
CAL005	*Betula pubescens*	Root	-28.9	54.8	46.7	0.9
CAL005	Soil Sample E		-29.0	18.5	43.5	2.4
CAL005	Soil Sample F		-28.2	18.6	29.2	1.6
CAL005	*Betula pubescens*	Twig	-30.6	91.4	44.9	0.5

Table D1: Calthorpe $\delta^{13}C$ and C/N ratios and %C, %N for sampled plant and soil material.

Site No:	Species	Material type	$\delta^{13}C$ (‰)	C/N	%C	%N
WH001	*Alnus glutinosa*	Leaf	-32.1	14.7	47.3	3.2
WH001	*Alnus glutinosa*	Root	-30.4	66.5	46.5	0.7
WH001	*Rubus fruticosus*	Stem	-33.9	66.5	42.1	0.6
WH001	*Alnus glutinosa*	Twig	-29.9	63.1	46.0	0.7
WH001	Soil sample A		-28.1	13.1	10.0	0.8
WH002	*Alnus glutinosa*	Leaf	-33.4	14.5	44.9	3.1
WH002	*Rubus fruticosus*	Leaf	-35.3	20.8	41.8	2.0
WH002	*Alnus glutinosa*	Twig	-33.9	51.1	46.2	0.9
WH002	Soil sample B		-28.9	14.7	16.3	1.1
WH002	Soil sample C		-28.4	11.6	16.6	1.4
WH003	*Eupatorium cannabinum*	Leaf	-32.0	14.1	41.0	2.9
WH005	*Alnus glutinosa*	Twig	-33.3	48.1	48.3	1.0
WH005	*Salix cinerea*	Leaf	-29.9	21.0	47.7	2.3
WH005	*Salix cinerea*	Twig	-30.0	64.6	42.0	0.6
WH006	Soil sample D		-28.6	14.2	9.5	0.7
WH006	Soil sample E		-28.5	13.0	11.1	0.9

Table D2: Wheatfen $\delta^{13}C$ and C/N ratios and %C, %N for sampled plant and soil material.

Site No:	Species	Material type	$\delta^{13}C$ (‰)	C/N	%C	%N
OHF001	*Alnus glutinosa*	Leaf	-31.6	15.5	48.6	3.1
OHF001	*Salix fragilis*	Leaf	-31.3	19.3	43.2	2.2
OHF001	*Urtica dioica*	Leaf	-32.0	11.3	33.1	2.9
OHF001	*Urtica dioica*	Stem	-31.3	41.1	40.6	1.0
OHF001	*Salix fragilis*	Twig	-31.0	61.4	46.1	0.8
OHF001	Soil sample A		-26.5	14.0	4.7	0.3
OHF001	*Alnus glutinosa*	Twig	-31.5	56.7	45.6	0.8
OHF003	Soil sample B		* see note	12.8	4.6	0.4
OHF004	*Alnus glutinosa*	Leaf	-31.0	12.8	47.8	3.7
OHF004	*Rubus fruticosus*	Leaf	-31.8	14.4	42.9	3.0
OHF004	*Salix fragilis*	Leaf	-31.0	19.9	44.5	2.2
OHF004	*Urtica dioica*	Leaf	-31.9	9.7	33.0	3.4
OHF004	*Alnus glutinosa*	Root	-29.2	47.7	44.9	0.9
OHF004	*Salix fragilis*	Root	-28.3	88.9	43.0	0.5
OHF004	*Rubus fruticosus*	Stem	-31.3	35.5	43.3	1.2
OHF004	*Urtica dioica*	Stem	-32.0	26.8	40.5	1.5
OHF004	*Alnus glutinosa*	Twig	-30.8	48.5	47.1	1.0
OHF005	Soil sample C		-28.5	12.1	5.6	0.5
OHF006	*Alnus glutinosa*	Leaf	-32.4	16.4	47.8	2.9
OHF006	*Salix fragilis*	Leaf	-29.2	20.1	46.8	2.3
OHF006	*Alnus glutinosa*	Twig	-32.9	59.3	46.0	0.8
OHF006	*Salix fragilis*	Twig	-28.7	50.0	43.5	0.9
OHF006	*Salix fragilis*	Twig	-28.6	64.0	46.2	0.7
OHF006	Soil sample D		-28.6	13.6	7.0	0.5
OHF006	Soil sample E		-28.1	11.2	4.8	0.4

Table D3: Old House Farm $\delta^{13}C$ and C/N ratios and %C, %N for sampled plant and soil material. Note: OHF Soil Sample – not enough material tested for $\delta^{13}C$ ratio.

Site No:	Species	Material type	$\delta^{13}C$ (‰)	C/N	%C	%N
CF001	*Alnus glutinosa*	Leaf	-32.4	16.0	46.4	2.9
CF001	*Dryopteris dilatata*	Leaf	-29.4	17.3	44.8	2.6
CF001	*Rubus fruticosus*	Leaf	-33.1	15.8	43.3	2.7
CF001	*Salix cinerea*	Leaf	-31.5	20.4	46.6	2.3
CF001	*Urtica dioica*	Leaf	-30.7	10.7	31.6	3.0
CF001	*Alnus glutinosa*	Root	-31.1	47.0	47.2	1.0
CF001	*Salix cinerea*	Root	-29.1	41.2	45.4	1.1
CF001	*Rubus fruticosus*	Stem	-26.6	63.7	42.3	0.7
CF001	*Urtica dioica*	Stem	-30.8	31.8	40.9	1.3
CF001	*Alnus glutinosa*	Twig	-30.2	47.1	43.5	0.9
CF001	Soil Sample A		-30.0	20.2	41.9	2.1
CF001	*Salix cinerea*	Twig	-27.9	76.9	39.1	0.5
CF002	Soil Sample B		-29.9	12.4	34.1	2.8
CF003	*Alnus glutinosa*	Twig	-31.7	61.8	46.6	0.8
CF003	*Alnus glutinosa*	Leaf	-31.8	17.8	46.1	2.6
CF003	*Dryopteris dilatata*	Leaf	-30.0	16.0	46.1	2.9
CF003	*Urtica dioica*	Leaf	-31.9	9.9	34.5	3.5
CF003	*Alnus glutinosa*	Root	-29.6	52.3	44.4	0.8
CF003	*Urtica dioica*	Stem	-31.4	35.1	42.3	1.2
CF003	*Alnus glutinosa*	Twig	-31.0	53.4	44.8	0.8
CF003	Soil Sample C		-29.1	13.9	34.2	2.5
CF004	*Rubus fruticosus*	Leaf	-33.5	17.2	44.2	2.6
CF004	*Salix alba*	Leaf	-29.2	17.3	44.7	2.6
CF004	*Salix cinerea*	Leaf	-32.3	20.8	46.5	2.2
CF004	*Rubus fruticosus*	Stem	-32.2	52.9	43.7	0.8
CF004	*Salix alba*	Twig	-29.2	46.7	45.0	1.0
CF004	*Salix cinerea*	Twig	-30.9	78.5	45.7	0.6

CF004	Soil Sample D		-30.1	17.8	38.4	2.2
CF005	*Rubus fruticosus*	Stem	-32.4	72.3	43.5	0.6
CF005	*Alnus glutinosa*	Leaf	-32.7	15.7	45.2	2.9
CF005	*Alnus glutinosa*	Twig	-29.0	46.8	46.7	1.0
CF005	*Alnus glutinosa*	Twig	-30.0	68.1	46.3	0.7
CF005	Soil Sample E		-29.2	14.2	4.4	0.3

Table D4: Carter's Farm $\delta^{13}C$ and C/N ratios and %C, %N for sampled plant and soil material.

Site No:	Species	Material type	$\delta^{13}C$ (‰)	C/N	%C	%N
RSM001	*Aster tripolium basal leaves*	Leaf	-27.0	21.8	24.3	1.1
RSM001	*Seriphidium maritimum*	Leaf	-24.7	23.6	26.1	1.1
RSM001	*Aster tripolium*	Leaf	-26.9	23.8	33.0	1.4
RSM001	*Aster tripolium*	Stem	-25.5	113.3	38.1	0.3
RSM001	*Seriphidium maritimum*	Stem	-27.1	61.8	42.6	0.7
RSM001	*Festuca rubra*	Grass	-25.8	44.9	39.4	0.9
RSM001	Soil Sample A		-13.7	18.3	4.0	0.2
RSM002	*Aster tripolium basal leaves*	Stem	-32.3	56.0	43.1	0.8
RSM004	Soil Sample B		-17.5	14.5	3.8	0.3
RSM004	*Seriphidium maritimum*	Leaf	-26.1	21.8	22.4	1.0
RSM006	*Festuca rubra*	Grass	-25.5	39.1	40.0	1.0
RSM006	*Limonium vulgare*	Stem	-27.0	46.2	42.5	0.9
RSM006	*Limonium vulgare*	Leaf	-26.0	17.0	38.4	2.3
RSM007	*Suaeda verna*	Leaf	-27.6	33.7	26.1	0.8
RSM008	*Festuca rubra*	Grass	-24.6	17.2	30.0	1.7
RSM009	*Salicornia ramossisima*	Stem	-25.3	18.2	24.1	1.3
RSM011	Soil Sample C		-16.8	16.0	4.0	0.2
RSM011	*Salicornia ramossisima*	Stem	-28.1	19.3	25.6	1.3
RSM012	*Festuca rubra*	Grass	-24.4	15.8	25.3	1.6
RSM012	*Salicornia fragilis*	Stem	-26.5	20.7	20.2	1.0
RSM014	*Salicornia fragilis*	Stem	-27.3	15.5	29.0	1.9
RSM014	Soil Sample D		-23.6	21.8	9.3	0.4
RSM017	*Seriphidium maritimum*	Leaf	-25.8	16.8	22.4	1.3

Table D5: Rye Saltmarsh $\delta^{13}C$ and C/N ratios and %C, %N for sampled plant and soil material.

Appendix E

Hope Farm $\delta^{13}C$ and C/N ratios, %C and %N.

My Code	Depth start (cms)	Depth finish (cms)	$\delta^{13}C$ (‰)	%C	%N	C/N
1	172	173	-26.9801	2.739	0.186	14.72581
2	173	174	-25.3746	2.268	0.16	14.175
3	174	175	-27.0809	2.289	0.151	15.15894
4	175	176	-27.2909	5.491	0.283	19.40283
5	176	177	-27.5729	5.768	0.314	18.36943
6	177	178	-27.8184	7.814	0.403	19.38958
7	186	187	-27.9368	32.311	2.034	15.88545
8	187	188	-28.2775	39.822	2.343	16.99616
9	188	189	-28.3986	37.548	2.348	15.99148
10	189	190	-28.328	44.425	1.89	23.50529
11	190	191	-27.7116	48.641	0.994	48.93461
12	191	192	-28.1265	43.602	1.306	33.38591
13	192	193	-28.1352	43.64	1.704	25.61033
14	193	194	-27.8598	48.051	1.258	38.19634
15	194	195	-28.0625	47.221	1.47	32.12313
16	195	196	-28.8072	45.87	2.116	21.67769
17	196	197	-28.0887	44.6	2.035	21.91646
18	197	198	-28.0479	46.483	1.932	24.05952
19	198	199	-27.3817	43.263	1.253	34.52753
20	199	200	-28.4463	46.281	1.683	27.49911
21	200	201	-27.9831	45.422	1.427	31.83041
22	201	202	-27.1601	44.824	0.445	100.7281
23	202	203	-29.3492	52.363	0.97	53.98247
24	203	204	-28.5582	46.978	1.563	30.0563

25	204	205	-28.3503	48.131	1.361	35.36444
26	205	206	-27.9126	45.447	0.664	68.44428
27	206	207	-27.9105	44.956	1.545	29.09773
28	207	208	-27.053	39.881	1.198	33.28965
29	208	209	-27.8229	45.119	2.352	19.18325
30	209	210	-27.6936	47.692	2.282	20.89921
31	218	219	-27.7647	47.509	1.244	38.19051
32	219	220	-27.9663	44.942	1.614	27.84511
33	220	221	-27.6025	48.407	1.253	38.63288
34	221	222	-28.1236	48.606	1.207	40.27009
35	222	223	-28.9099	47.367	1.847	25.64537
36	223	224	-28.9215	46.494	2.039	22.80235
37	224	225	-29.093	48.76	1.688	28.88626
38	225	226	-28.7909	49.383	1.637	30.16677
39	226	227	-28.7838	50.021	1.323	37.80877
40	227	228	-28.3449	46.672	1.648	28.32039
41	228	229	-29.0126	42.152	1.63	25.86012
42	229	230	-28.0997	49.56	1.108	44.72924
43	230	231	-28.9193	45.102	1.723	26.17644
44	231	232	-29.048	43.107	1.681	25.64366
45	232	233	-28.7109	46.468	1.823	25.48985
46	233	234	-28.3094	47.752	1.814	26.32415
47	234	235	-28.9231	47.715	2.279	20.93681
48	235	236	-29.2087	45.713	2.12	21.56274
49	236	237	-29.5277	47.875	2.282	20.9794
50	237	238	-29.6164	47.767	2.111	22.62766
51	238	239	-29.1402	47.338	1.937	24.43882
52	239	240	-29.1264	47.083	2.038	23.10255

53	240	241	-29.3718	48.784	1.944	25.09465
54	241	242	-28.4714	53.091	1.498	35.44126
55	242	243	-28.9164	46.993	1.644	28.58455
56	243	244	-29.0615	46.191	2.313	19.97017
57	244	245	-28.7399	45.417	1.381	32.88704
58	245	246	-28.4017	49.245	1.56	31.56731
59	254	255	-26.7521	49.071	0.984	49.8689
60	255	256	-28.343	49.211	2.331	21.11154
61	256	257	-28.245	47.008	2.521	18.64657
62	257	258	-28.2498	44.916	2.298	19.54569
63	258	259	-28.2365	53.817	1.253	42.95052
64	259	260	-28.7982	47.498	1.86	25.53656
65	260	261	-27.9037	51.311	1.734	29.59112
66	261	262	-26.6626	49.484	1.124	44.02491
67	262	263	-29.0936	50.281	2.515	19.99245
68	263	264	-29.2287	46.551	2.119	21.96838
69	264	265	-28.5786	44.57	2.185	20.39817
70	265	266	-28.1474	47.615	1.853	25.69617
71	266	267	-28.7344	45.463	1.691	26.88527
72	267	268	-28.3395	48.32	2.079	23.24194
73	268	269	-29.3143	48.461	2.552	18.98942
74	269	270	-29.2574	48.627	2.475	19.64727
75	270	271	-29.1734	45.184	2.068	21.84913
76	271	272	-28.4053	47.261	2.078	22.7435
77	272	273	-28.9068	47.657	2.408	19.79111
78	273	274	-28.958	47.001	2.354	19.96644
79	274	275	-27.7978	51.143	1.734	29.49423
80	275	276	-29.203	48.353	2.282	21.18887

81	276	277	-29.4005	48.787	1.766	27.62571
82	277	278	-29.1131	49.833	1.663	29.96572
83	278	279	-29.0221	46.813	2.189	21.38556
84	279	280	-29.1774	46.711	2.162	21.60546
85	280	281	-29.1283	45.68	2.206	20.70716
86	281	282	-28.1852	41.996	1.73	24.27514
87	286	287	-28.7868	49.86	1.922	25.94173
88	287	288	-28.8619	46.27	2.367	19.54795
89	288	289	-28.2228	47.391	2.348	20.18356
90	289	290	-28.7784	46.95	2.332	20.13293
91	290	291	-28.8566	43.661	2.231	19.57015
92	291	292	-28.8036	49.13	2.063	23.81483
93	292	293	-28.6643	46.462	2.456	18.91775
94	293	294	-28.0671	53.986	1.885	28.63979
95	300	301	-27.1715	10.14	0.668	15.17964
96	301	302	-26.2933	3.322	0.261	12.72797
97	302	303	-26.2887	5.687	0.451	12.60976

Table E1: Hope Farm $\delta^{13}C$ and C/N ratios, %C and %N.

Appendix F

Little Cheyne Court $\delta^{13}C$ and C/N ratios, %C and %N.

My Code	Depth start (cms)	Depth finish (cms)	$\delta^{13}C$ (‰)	%C	%N	C/N
98	225	226	-27.5	48.3	1.0	47.3
99	226	227	-26.7	47.7	0.9	52.3
100	227	228	-27.1	44.2	0.9	47.5
101	228	229	-27.2	48.0	1.0	46.1
102	229	230	-26.9	48.7	1.0	46.6
103	230	231	-26.9	47.5	1.0	48.9
104	231	232	-27.7	49.5	1.0	48.5
105	232	233	-27.3	48.4	0.8	57.7
106	233	234	-27.7	48.1	1.1	43.3
107	234	235	-27.6	44.8	1.3	33.9
108	235	236	-27.4	50.4	1.1	45.9
109	236	237	-27.5	51.1	1.1	48.3
110	237	238	-27.6	50.2	0.9	54.0
111	238	239	-27.0	46.7	0.7	66.0
112	239	240	-27.5	50.0	1.0	52.3
113	240	241	-27.5	50.4	1.1	46.9
114	241	242	-27.7	51.3	1.2	42.4
115	242	243	-27.0	49.8	1.0	52.3
116	243	244	-26.3	49.0	1.0	49.3
117	244	245	-26.5	42.6	0.9	49.3
118	245	246	-26.7	44.6	0.9	49.3
119	246	247	-27.0	50.6	1.1	47.3
120	247	248	-27.0	50.3	1.1	46.6
121	248	249	-26.7	49.2	1.0	50.2
122	249	250	-26.6	48.4	0.9	55.5

123	250	251	-27.7	51.8	0.9	60.5
124	251	252	-26.2	47.8	0.9	55.0
125	252	253	-27.0	49.2	1.0	49.2
126	253	254	-29.6	51.3	1.5	33.4
127	254	255	-25.9	48.4	0.8	60.4
128	255	256	-25.7	46.4	0.6	82.1
129	256	257	-25.4	46.2	0.4	117.3
130	257	258	-25.9	47.4	0.6	85.8
131	258	259	-28.0	47.5	2.1	22.6
132	259	260	-26.4	48.5	0.8	62.7
133	260	261	-26.3	20.5	0.6	34.4
134	261	262	-26.6	49.5	0.9	54.9
135	262	263	-26.1	47.2	0.8	60.3
136	263	264	-25.5	47.6	0.6	81.0
137	264	265	-26.2	47.0	0.6	82.9
138	265	266	-26.4	48.6	0.7	67.8
139	266	267	-27.1	47.4	0.7	64.7
140	267	268	-27.7	47.4	1.3	35.7
141	268	269	-26.0	50.9	0.8	67.5
142	269	270	-25.3	51.1	0.6	84.0
143	270	271	-26.3	48.8	0.8	60.9
144	271	272	-26.3	47.9	0.7	70.0
145	272	273	-26.0	47.2	0.5	99.3
146	273	274	-27.2	51.3	0.7	75.5
147	274	275	-27.7	48.8	0.8	63.5
148	275	276	-27.8	49.8	0.8	61.8
149	284	285	-27.0	52.2	1.7	31.3
150	285	286	-27.3	51.8	1.7	30.9

151	286	287	-27.5	50.7	1.7	30.5
152	287	288	-27.4	51.5	1.4	37.6
153	288	289	-28.9	47.9	2.2	22.0
154	289	290	-27.2	50.9	1.1	46.1
155	290	291	-27.4	51.0	1.1	45.8
156	291	292	-27.5	49.4	1.1	44.7
157	293	294	-27.1	51.1	1.1	46.2
158	294	295	-27.2	50.5	1.1	44.2
159	295	296	-26.9	50.1	1.2	41.1
160	296	297	-25.9	50.9	1.1	47.9
161	297	298	-25.3	50.7	0.9	55.0
162	298	299	-26.6	49.8	1.1	45.0
163	299	300	-26.3	50.9	1.2	41.7
164	300	301	-25.8	34.3	0.8	44.8
165	301	302	-26.8	5.1	0.1	48.2
166	302	303	-26.1	51.6	1.0	52.2
167	303	304	-25.5	48.1	0.8	57.8
168	304	305	-27.1	50.9	1.0	51.5
169	305	306	-27.5	52.4	1.2	43.0
170	306	307	-27.5	50.5	1.4	35.0
171	307	308	-27.5	50.0	1.1	44.5
172	308	309	-26.2	51.7	0.9	55.2
173	309	310	-27.1	47.1	1.1	44.8
174	311	312	-27.8	50.5	1.2	43.0
175	312	313	-27.2	51.7	1.0	51.3
176	313	314	-27.4	50.9	1.2	43.3
177	314	315	-27.7	51.4	1.1	47.6
179	317	318	-27.8	48.6	2.4	20.5

180	318	319	-27.7	50.0	1.1	44.9
181	319	320	-27.2	51.4	1.3	41.0
182	320	321	-27.5	51.8	1.2	43.6
183	321	322	-28.2	53.4	1.2	45.8
184	322	323	-27.4	52.2	1.3	40.4
185	323	324	-27.7	52.6	1.1	49.2
186	324	325	-27.5	45.3	1.0	44.6
187	325	326	-27.6	52.2	1.4	36.0
188	326	327	-26.2	47.9	1.2	41.4
189	327	328	-25.7	50.0	0.9	52.6
190	328	329	-27.0	51.3	1.0	48.9
191	329	330	-28.8	52.2	1.4	37.4
192	330	331	-28.4	50.4	1.0	50.0
193	331	332	-28.0	51.0	1.1	47.7
194	332	333	-28.6	53.7	1.0	53.9
195	333	334	-28.4	52.7	1.0	51.7
196	342	343	-29.1	48.6	1.9	25.9
197	343	344	-29.6	49.1	1.4	35.2
198	344	345	-29.0	52.2	1.8	28.3
199	345	346	-29.0	51.4	1.7	29.5
200	347	348	-28.7	51.4	1.8	28.2
201	348	349	-29.2	51.5	1.8	29.1
202	349	350	-29.1	52.2	1.9	27.1
203	350	351	-28.7	51.3	2.1	24.4
204	351	352	-29.5	50.4	1.5	33.1
205	352	353	-29.0	51.0	1.7	29.6
206	353	354	-28.5	50.9	1.7	29.6
207	354	355	-28.3	51.3	1.6	31.7

208	355	356	-28.3	51.4	1.7	29.6
209	356	357	-29.5	49.9	1.0	50.6
210	357	358	-28.3	52.3	1.5	34.2
211	358	359	-28.5	46.8	1.4	34.5
212	359	360	-28.1	51.9	1.5	34.6
213	360	361	-27.2	47.5	0.8	62.9
214	361	362	-28.0	50.3	1.7	29.5
215	362	363	-28.3	51.1	1.8	28.2
216	363	364	-27.9	43.2	1.1	38.6
217	364	365	-28.4	51.3	1.7	29.7
218	365	366	-28.1	49.7	2.1	24.1
219	367	368	-28.2	51.5	2.0	25.4
220	368	369	-28.3	51.1	2.1	24.8
221	369	370	-27.6	50.7	2.0	25.2
222	370	371	-28.2	48.9	2.3	20.8
223	371	372	-27.8	53.0	1.5	34.9
224	372	373	-28.0	53.2	1.4	39.1
225	373	374	-28.7	49.6	1.3	39.5
226	374	375	-28.2	53.1	1.4	37.0
227	375	376	-28.4	50.7	1.3	38.4
228	385	386	-27.1	31.3	1.4	22.6
229	386	387	-27.1	32.2	1.5	21.5
230	387	388	-26.9	15.9	0.6	25.1
231	388	389	-26.9	8.6	0.4	22.8
232	389	390	*see note	3.3	0.2	21.3
233	390	391	-26.6	5.4	0.2	22.4
234	391	392	-26.9	2.9	0.2	18.6

Table F1: Little Cheyne Court $\delta^{13}C$ and C/N ratios, %C and %N. Note: My Code No: 232, no $\delta^{13}C$ ratio since not enough material tested.

Appendix G

Difference between Holocene and contemporary atmospheric CO_2 $\delta^{13}C$ ratios.

Year	Add	Year	Add	Year	Add	Year	Add
1850	0.01	**1888**	0.18	**1926**	0.35	**1964**	0.58
1851	0.02	**1889**	0.18	**1927**	0.35	**1965**	0.61
1852	0.02	**1890**	0.19	**1928**	0.36	**1966**	0.63
1853	0.03	**1891**	0.19	**1929**	0.36	**1967**	0.66
1854	0.03	**1892**	0.2	**1930**	0.37	**1968**	0.69
1855	0.03	**1893**	0.2	**1931**	0.37	**1969**	0.72
1856	0.04	**1894**	0.21	**1932**	0.38	**1970**	0.75
1857	0.04	**1895**	0.21	**1933**	0.38	**1971**	0.77
1858	0.05	**1896**	0.22	**1934**	0.38	**1972**	0.8
1859	0.05	**1897**	0.22	**1935**	0.39	**1973**	0.83
1860	0.06	**1898**	0.22	**1936**	0.39	**1974**	0.86
1861	0.06	**1899**	0.23	**1937**	0.4	**1975**	0.89
1862	0.07	**1900**	0.23	**1938**	0.4	**1976**	0.92
1863	0.07	**1901**	0.24	**1939**	0.41	**1977**	0.94
1864	0.07	**1902**	0.24	**1940**	0.41	**1978**	0.97
1865	0.08	**1903**	0.25	**1941**	0.42	**1979**	1
1866	0.08	**1904**	0.25	**1942**	0.42	**1980**	1.03
1867	0.09	**1905**	0.26	**1943**	0.42	**1981**	1.06
1868	0.09	**1906**	0.26	**1944**	0.43	**1982**	1.08
1869	0.1	**1907**	0.26	**1945**	0.43	**1983**	1.11
1870	0.1	**1908**	0.27	**1946**	0.44	**1984**	1.14
1871	0.11	**1909**	0.27	**1947**	0.44	**1985**	1.17
1872	0.11	**1910**	0.28	**1948**	0.45	**1986**	1.2
1873	0.11	**1911**	0.28	**1949**	0.45	**1987**	1.22
1874	0.12	**1912**	0.29	**1950**	0.46	**1988**	1.25
1875	0.12	**1913**	0.29	**1951**	0.46	**1989**	1.28
1876	0.13	**1914**	0.3	**1952**	0.46	**1990**	1.31
1877	0.13	**1915**	0.3	**1953**	0.47	**1991**	1.34
1878	0.14	**1916**	0.3	**1954**	0.47	**1992**	1.37
1879	0.14	**1917**	0.31	**1955**	0.48	**1993**	1.39
1880	0.15	**1918**	0.31	**1956**	0.48	**1994**	1.42
1881	0.15	**1919**	0.32	**1957**	0.49	**1995**	1.45
1882	0.15	**1920**	0.32	**1958**	0.49	**1996**	1.48
1883	0.16	**1921**	0.33	**1959**	0.5	**1997**	1.51
1884	0.16	**1922**	0.33	**1960**	0.5	**1998**	1.53
1885	0.17	**1923**	0.34	**1961**	0.51	**1999**	1.56
1886	0.17	**1924**	0.34	**1962**	0.52	**2000**	1.59
1887	0.18	**1925**	0.34	**1963**	0.55	**2001**	1.62
						2002	1.65
						2003	1.67
						2004	1.69
						2005	1.72
						2006	1.75

Table G1: $\delta^{13}C$ ‰ to add to contemporary atmospheric CO_2 from 1850 to present, based on McCarroll and Loader (2004).

Appendix H

Mixing model to assess the relative contribution of plant species in alder-dominated woodlands.

$$x = \frac{0.75(\%Al + \%Bl + \%Sl) + 0.25(\%At + \%Bt + \%St)}{\%ABS}$$

where *%Al*, *%Bl* and *%Sl* are the total biomass of *Alnus glutinosa, Betula* spp. and *Salix* spp. respectively (2 x upper canopy + 1 x lower canopy) multiplied by the mean, minimum and maximum leaf $\delta^{13}C$ for their respective species. *%At*, *%Bt* and *%St* are the total biomass of *A. glutinosa*, *Betula* spp. and *Salix* spp. respectively multiplied by the mean, minimum and maximum twig $\delta^{13}C$ for their respective species. This figure is then divided by the total biomass of *Alnus, Betula* and *Salix*.

For example in the Carter's Farm (see Appendix A4) CF001 sub-site *Alnus glutinosa* forms 100% of the upper canopy, and 15% of the lower canopy, while *Salix cinerea* forms 15% of the lower canopy (70% of the lower canopy is absent).

Therefore *%A* = 2(%Upper canopy) +1(Lower canopy)

%A = 2(100) + (15)

***%A* = 215**

Similarly *%S* = 2(0) + 1(15)

***%S* = 15**

Since there is no *Betula* present, *%B* = 0

%ABS = 215 + 15 + 0 = **230**.

The mean *Alnus glutinosa* leaf $\delta^{13}C$ at Carter's Farm is **−32.3‰**, and the mean *A. glutinosa* twig $\delta^{13}C$ at Carter's Farm is **−30.4‰**. Similarly the *Salix* spp. leaf $\delta^{13}C$ is **−31.0‰** and the twig $\delta^{13}C$ is **−29.3‰**.

Therefore:

$$x = \frac{0.75((215)(-32.3) + (15)(-31.0)) + 0.25((215)(-30.4) + (15)(-29.3))}{230}$$

$$x = \frac{0.75(-7409.5) + 0.25(6975.5)}{230}$$

$$x = \frac{-5557 - 1744}{230}$$

$$x = -31.7$$

Thus for the Carter's Farm CF001 sub-site the predicted mean $\delta^{13}C$ of the contemporary soil, based on the $\delta^{13}C$ of the investigated tree species, is −31.7‰